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An Investigation of the Mechanism of Emulsion Stabilization by 4-Hydroxy-6-Methyl-1,3,3a,7-Tetraazaindene

Eddie Rising

AN INVESTIGATION OF THE MECHANISM OF EMULSION STABILIZATION BY 4-HYDROXY-6-METHYL-1,3,3a,7-TETRAAZAINDENE

by

Eddie J. Rising, II

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the School of Photographic Arts and Sciences of the Rochester Institute of Technology

June, 1972

Thesis adviser: Professor Burt H. Carroll

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An Abstract

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ABSTRACT

There is considerable speculation in literature as to the mechanism of photographic emulsion stabilization by 4-hydroxy-6-methyl-1,3,3a, 7-tetraazaindene, (Aza).

Aza is important as a stabilizer because, unlike the heterocyclic mercaptans, it causes no desensitization when the emulsion is processed in the commonly used MQ developing agents. The mercaptans are strongly adsorbed, whereas Aza is weakly adsorbed on silver halide. Therefore, there has been speculation that the stabilization mechanism of Aza is distinctly different from that of the mercaptans.

For this work, Aza was tested as an antifogging agent and development restrainer along with KBr, as a reference, in two developers which function at emulsion pH, (6 to 7): (1) Amidol at pH 6, 7, and 8, and (2) the ferrous ethylenediaminetetraacetate (EDTA) complex ion at pH 4.5, 7.0, 8.5, and 10.0. KODAK Fine Grain Positive Film, 5302, was used with both developers, and KODAK PANATOMIC-X Fine Grain Film, 5060, was used only with Fe-EDTA. Aza and KBr were compared sensitometrically for effects on fog, contrast index, and exposure index. This sensitometric evaluation comprises Section 1 of this work.

The evaluation yielded evidence that at the pH of photographic emulsions, (near 7), and in concentrations of Aza normally used in the emulsions, (1 to 2 grams/mol Ag X), Aza, like KBr, was both a restrainer and an antifoggant during the development of the 5302 Film by both Amidol and Fe-EDTA. PANATOMIC-X Film, 5060, processed in Fe-EDTA gave similar results. The restraint of development by Aza decreased at pH values above 8.5.

This evidence and the fact that Aza is adsorbed on the grains of the emulsion to the same extent as the mercaptans, when present in amounts normally used, remove the necessity for assuming two distinctly different mechanisms of emulsion stabilization. The fact that Aza caused no desensitization or restraining action during development at the high pH of the commonly used MQ developers is explained by its desorption from the development centers.

Section 2 of this work consists of a study in determining if there was an increase in the adsorption of Aza on silver bromide as a result of any effective increase in the concentration of Aza after drying the emulsion.

An adsorption equilibrium exists between 1, 1'-diethyl-2, 2'-cyanine iodide dye and Aza on silver bromide in the emulsion. Because the displacement, or deaggregation, of dye by Aza was evidenced by a decrease in the J-band strength of the dye, this decrease in J-band absorption at 575 nm was a convenient measure of the equilibrium. Aza not only decreased the J-band strength of the dye but also caused the appearance of two bands, identified as unaggregated dye in gelatin, one with maximum at 495 nm and the other near 530 nm. This is evidence that Aza not only deaggregated the dye but also displaced it from the AgBr.

The analysis was made with a Beckman DK-2A Spectrophotometer which measured total reflectance and transmittance by means of an integrating sphere over the wavelength range 380 to 730 nm. From these data, absorption was calculated for the dye in the presence and the absence of Aza both wet and dry.

The results of Section 2 of this work are evidence that the adsorption equilibrium between Aza and dye on silver bromide did not significantly change on drying the emulsion in spite of the change in the concentration of Aza from the wet to the dry emulsion.

Abstract approved: ,thesis adviser

,title and department

,date

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INTRODUCTION

Various organic compounds, known as emulsion stabilizers and anti-fogging agents (development restrainers), are widely employed in modern photographic emulsions and in the development of photographic material. The majority of these organic substances are heterocyclic compounds with nitrogen or sulfur in the ring. Emulsion stabilizers are chemical agents used to delay the formation of fog during the second digestion (after-ripening) of the emulsion making process, or are added to the emulsion prior to coating to stabilize it during storage. Antifogging agents are chemical compounds which retard the reduction of unexposed silver halide in development. The mechanism according to which antifoggants operate is not sharply delineated from that of the emulsion stabilizers. Antifoggants added to the emulsion normally act as emulsion stabilizers, but stabilizers are not necessarily antifoggant in development.

Emulsion fog formed during storage is caused by a slow continuation of the chemical sensitization process as shown by Carroll, Hubbard, and Kretchman.[1] In the chemical sensitization of a simple emulsion, sensitivity nuclei in different sizes and number are formed on the surface of the silver halide grains during the digestion after washing. These sensitivity specks can subsequently provide either electron or hole traps on exposure. "Over-ripening" may produce too many or too large nuclei such that some emulsion grains develop spontaneously without exposure. In practical emulsion manufacture, it is impossible to consume all the reducing agents and active sulfur compounds present in the gelatin in the ripening phase, and sensitization will continue at a slower rate even after coating and

drying the emulsion and during storage. This continuing process of sensitization beyond the region of optimum speed may result in emulsion fog. The primary purpose of the stabilizer is to counteract this continuing process which will eventually lead to unacceptable fog.

Carroll and Hubbard[2] have shown that the adjustment of pH and pAg to predetermined values is essential to maintain stability of the emulsion during storage. Low pAg results in a rapid rate of continued sensitization during storage. This rate can be reduced to a low level optimum for storage by controlling the bromide as shown by Forsgard.[3]

Antifoggants restrain the formation of developer fog during photographic development, retard the development itself, and, when added to the photographic emulsion, normally behave as emulsion stabilizers.

As previously mentioned, there is no clearly defined distinction between the mechanisms according to which emulsion stabilizers and antifoggants operate. There have been several mechanisms suggested in the literature for both cases. However, both are usually explained in terms of the affinity of the compounds for silver ions and the adsorption of the agents or their stable silver salts on silver halide[4,5,9] or the sensitivity nuclei.[23,24,27]

This substantiates an early suggestion by Carroll and Hubbard[6]. Matthies and Wendt[7] claimed as an antifoggant any compound which forms an insoluble silver salt with a solubility the same or less than that of silver chloride. They also said that such compounds

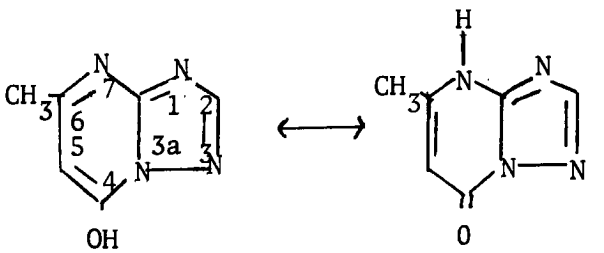
are, in general, adsorbed on silver halide. They proposed this mechanism in a patent and did not actually prove it. The work of Matthies and Wendt was extended to a variety of heterocyclic organic silver-ion complexing agents by Faerman[8] and Kikuchi[9] and their collaborators. Faerman[8,10] indicated that a compound can be both a stabilizer and an antifoggant even though its silver salt solubility is higher than that of the emulsion grains.

From a physico-chemical point of view a photographic emulsion must be considered as a multi-component heterogeneous system whose components are in a complex chemical and adsorption interaction. The experimental evidence previously cited seems to indicate that it is adsorption or lack of adsorption on the silver-halide crystal that governs the mode of action of antifoggants and emulsion stabilizers. Adsorption on silver halide is dependent on pH and pAg.[11] Faerman[8] has also shown that the silver salt solubility is pH dependent.

Organic stabilizers introduced by Wendt and co-workers[12,13] which have silver specific mercapto and imino groups forming solubility products in the range of that of the silver halides are strongly and extensively adsorbed on silver halide. Many of these compounds, such as benzotriazole, phenylmercaptotetrazole, and nitrobenzimidazole, have appeared in the journal and patent literature. These strongly adsorbed compounds increase the stability of photographic emulsions, but they also desensitize if too much is added. Hamilton and Brady[14] have shown that 1-phenyl-5-mercaptotetrazole decreased the number or life of mobile silver ions on the silver halide grains. These substances also act as antifoggants in development and may reduce sensitivity by restraining development. The fact that these compounds

are strongly adsorbed on the silver halide does not necessarily mean that the available surface is completely covered. Mees and James[5] point out that marked restraining and antifoggant action can be obtained with some compounds used in amounts so small that a complete monomolecular layer is impossible and suggest some form of selective adsorption. The degree of this selective adsorption depends on the chemical structure, pH, pAg, and concentration. Photographcially effective adsorption may be as low as 2-percent. Koseki[15] found that only 5 to 7-percent of the silver-halide crystal surface was covered by mercapto stabilizer when he determined the minimum amount of stabilizer necessary to decrease the rate of sensitization without a speed loss. He concluded that the stabilizer molecules became adsorbed on the silver halide crystal lattice at the most active sites.

One of the most effective of the organic heterocyclic stabilizers is 4-hydroxy-6-methyl-1, 3, 3a, 7-tetraazaindene (hereafter referred to as Aza)-a substance with empirical formula $C_6H_6N_4O$, a molecular weight of 150.1, and a structural formula consisting of two tautomeric forms:



Aza is a white crystalline powder, (M. P. 278°C)[24], which decomposes at high temperatures. It is soluble in polar solvents.

Aza is important as a stabilizer because, unlike the heterocyclic mercaptans, Aza causes no desensitization when the emulsion is processed in the developer, although Hamilton and Brady[14] found that Aza decreased the concentration of mobile silver ions in the emulsion in the same manner as the mercaptans.

Aza forms a stable silver salt with a solubility about that of silver chloride, but increasing with increasing pH.[8] Aza is not as strongly adsorbed as the mercaptans, which generally form silver salts less soluble than silver bromide. Birr[16], who discovered the photographic effect of Aza in 1936, found that at concentrations of the order used in practice not more than 5 to 10-percent is adsorbed in the liquid emulsion. However, because Aza is used at 1 to 2 grams/mol AgX, and the mercaptans are used at 5 to 20 mg/mol AgX, the amounts adsorbed are similar. Because of the weak adsorption of Aza on silver halide, there has been considerable speculation as to the mechanism of its action.

Birr[16,17,18] has shown that certain constituents of a developing solution tend to desorb Aza from silver and silver-sulfide development centers. The factors which influence this desorption of Aza are the developing agent itself, potassium bromide, sulfite, and alkalinity. It is this desorption that Birr contends is the reason for the inefficiency of Aza as an antifogging agent in the developer. Birr[16,17,18] has also indicated that 90-percent or more of the Aza in the emulsion under practical conditions is in the gelatin phase. However, under those conditions and in the amounts of Aza normally used, it is adsorbed to the same extent as the mercaptans.

Birr[19] has postulated two types of stabilizing mechanisms. In the first, the stabilizer is adsorbed and restrains the catalytic action of the nuclei by selective adsorption. The mercaptans which give marked emulsion stabilizing action in amounts (5 to 20 mg/mol AgX) that can cover only 1 to 2 percent of the silver halide surface, and which are strongly antifoggant in development at 10^{-5} mol/litre are examples of this type mechanism. In the second case, the stabilizer is not adsorbed and has no influence on development. Birr classifies the action of Aza as the second case because of its weak adsorption and its desorption from development centers at the high pH values commonly encountered in the standard MQ developing solutions. According to Birr[18], the favorable stabilizing effect of Aza is because it is held at a high level in the gelatin matrix adsorbed to the silver halide grain and acts primarily by inducing formation of sulfide in this layer away from actual contact with the silver halide crystal.

Meyer and Kleffe[20] have reported that Aza is desorbed from the emulsion grains and accumulates in the developer. They have extracted 97-percent of the Aza from the emulsion coating into the developing solution.

Berendsen[21a] and associates reported that Aza and thiosulfate had approximately equal energies of adsorption on the grains of a silver-bromide sol, (in the absence of gelatin), so that equilibrium was determined by concentration. Berendsen also found that Birr's weakly adsorbed Aza not only displaced the adsorbed thiosulfate from the silver-halide grains but also effectively inhibited silver-sulfide formation. In a later article, Berendsen[21b] reported that under emulsion conditions Aza retarded Ag_2S formation at low concentrations

of Aza, (up to 3 x 10^{-3} mol/mol AgX), and it accelerated Ag_2S formation at higher concentrations. Birr[25] found that Aza did not retard Ag_2S formation. Birr used very high Aza to AgBr ratios (that is, greater than 2.0 x 10^{-1} mol Aza/mol AgBr). However, his emulsions were relatively low in concentrations of Aza (that is, as low as 4 x 10^{-5} moles/litre). These conditions are widely different from those found in actual practice. Berendsen[21b] also reported, through centrifugation, that Ag_2S was found attached to the silver-halide grains. This result appears to be in conflict with Birr's[25] findings, namely that Aza induced the formation of Ag_2S in the gelatin matrix out of actual contact with the silver-halide crystals.

Chambers[22] compared the effects of twelve tetraazaindenes on the fog and speed stability of an experimental silver-iodobromide emulsion. Contrary to Birr, Chambers assumed that the stabilizing effect of Aza resulted from the adsorbed portion. Chambers had no proof that Aza or its derivatives were adsorbed on silver halide or reacted, (in the form of nonadsorbed silver salts) with sensitizers in the matrix. It is possible, however, that tetraazaindenes are adsorbed on silver or silver sulfide under certain conditions.

Using microcalorimetry, Wood[23] compared the saturation heats of adsorption of a series of commonly used stabilizers on AgCl, AgBr, and Ag_2S, (in the absence of gelatin). The majority of stabilizers analyzed did show a strong adsorption on silver sulfide. Wood concluded that the prepared silver sulfide carried a positive charge, enhancing adsorption of the stabilizers forming the stable silver salts. It was this adsorption of the stabilizers that Wood assumed prevented the growth of sensitivity specks in fog centers. Thompson[24]

has also proposed a mechanism similar to that of Wood. The fact that Wood observed the adsorption of Aza on silver sulfide again appears to be in conflict with Birr's[25] findings, namely that Aza accelerated silver-sulfide formation. Habu[26] observed both an accelerating and inhibiting effect by Aza on Ag_2S formation.

Since silver nuclei can be present in association with sensitivity centers, or in aggregates producing fog, or perhaps latent-image silver, Günther[27] has studied the adsorption of Aza and phenymercaptotetrazole on the silver nuclei. He observed that both stabilizers were adsorbed on the silver nuclei. Like Birr[17,18,28], Günther concludes that the inefficiency of Aza as an antifogging agent, is its desorption from the silver nuclei in the developer at high pH.

A very interesting result was reported by Faerman[8] in his investigation of the effect of Aza on the development process. His data on the effect of Aza on the rate of reduction of exposed silver bromide sols, (in the presence of gelatin), indicate that, at a pH of 5, Aza restrained the rate of reduction of the sols when processed in a developing solution utilizing Amidol as the developing agent. The extent of the restraint by Aza increased as the concentration of Aza was increased from 5×10^{-4} m/l to a concentration of 2×10^{-3} m/l, where the restraining activity of Aza became fairly constant.[10] This indicates the possible existence of a Langmuir-type adsorption isotherm. Faerman[29] has also shown that Aza influenced the process of recrystallization of silver bromide during the first ripening of a photographic emulsion, a factor that Birr[30] himself has shown to be significantly related to stabilization and antifogging agent activity.

It was observed that emulsion stabilizers interact with spectral sensitizers of the cyanine dye class adsorbed on the silver halide crystal surface. It is well known that stabilizers can disturb the orientation of adsorbed spectral sensitizers and thus weaken, or even destroy the J-band absorption of the dye.[31] Many dyes which are arranged on the surface of the silver halide crystal in a close packed array of molecules in an edge-on orientation show a strong, sharp absorption band displaced to long wavelengths from the absorption band of isolated adsorbed molecules. These bands appear at higher concentrations of adsorbed dye, and correspond in position, shape, and concentration-dependence to the bands characteristic of a certain state of multimolecular aggregation in aqueous solution, called the J-state of aggregation.[32] These new bands are referred to as J-bands.

Meyer and Polenz[31] have shown that Aza deaggregated or displaced certain carbocyanine dyes adsorbed on silver halide in an emulsion, as indicated by a decrease in the intensity of the J-band. They have also shown that it caused the disappearance of the J- and H-bands of many of the dyes in favor of the M-band. As previously mentioned, the J-band indicates the aggregated dye adsorbed on the silver halide grains in the emulsion. The H-band indicates the dye adsorbed on the silver halide in a different state of aggregation; and the M-band indicates the unaggregated dye.[33]

Further evidence that Aza is actually adsorbed to silver halide under certain conditions was reported by Shimada[34] and co-workers. Their data show the existence of a Langmuir-type adsorption isotherm of Aza on both the 100 and 111 grain structures of silver bromide. They concluded that the adsorption of Aza varied with the grain shapes of silver bromide and was dependent on the pAg of the solution. They

also found a good correlation between the amount of Aza adsorbed and its retarding action during development. They did not mention the pH of their emulsion, however most photographic emulsions have pH values in the vicinity of 6 or 7.

From the preceding discussion it is quite evident that there is no complete agreement on the mechanism of the outstanding class of stabilizers, the tetraazaindenes, so extensively studied. It should be emphasized that their mechanism as a class is not completely agreed upon. There have been many contradictions to Birr's two mechanism theory as previously described. Birr[28] himself has shown that Aza behaves similarly to the heterocyclic mercaptans if the alkyl radical in the six position contains a carbon chain length of four or more. He demonstrated the correlation between increasing adsorption, (as a result of increasing chain length), and increasing desensitization.

Two important variables were investigated in this work to provide further evidence as to the mechanism of stabilizing action by Aza. They were:

1. pH - as pointed out by Mees and James[5], selective adsorption is very dependent on pH. Faerman[8] has already shown that Aza appears to behave as an antifogging agent in developer at a pH of 5.

2. Concentration of Aza - Faerman's[8] data indicate that Aza restrains development if it is present at 10^{-5} mol/liter or greater. Aza is added to photographic emulsions in relatively large quantities, about 1 to 2 grams/mol AgX, in contrast to the mercaptans which are added in much smaller amounts, about 5 to 20 mg/mol AgX. Thus, if Aza possesses the Langmuir-

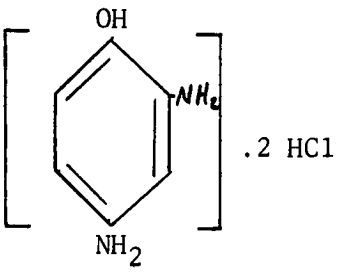
> type isotherm as reported by Shimada[34] and co-workers, it is probable that it is adsorbed to some extent on the silver halide grains at that high level of concentration. When the coated photographic emulsion dries, it changes from a gel containing about 6g gel/100g water to a dry gel with 10 to 15 percent water and shrinks to a fraction, about one-tenth, of its original coating thickness. This effect should consequently increase effective concentration of Aza by a factor of 10, thereby increasing the possibility of its adsorption on AgX.

The evidence previously cited indicates that Aza is adsorbed on the silver-halide grains of photographic emulsions at the pH of the emulsions, (6 or 7), when present in concentrations normally used (1 to 2 grams/mol AgX). Antifogging action and restraining action by Aza in the developer at emulsion pH may depend on the covering of active areas in unexposed and exposed grains by Aza. Since Aza is adsorbed to the same extent as the mercaptans, when present in amounts normally used, it seems unnecessary to assume two distinctly different mechanisms of emulsion stabilization. The fact that Aza causes no desensitization or antifogging action during normal development is explained by its desorption from the development centers at the pH values of the most-commonly-used developing solutions which usually have pH values much greater than 7.

To provide further evidence in support of this mechanism, Aza was tested as an antifogging agent at low pH values to minimize desorption. Various concentrations of Aza were also studied.

In order to show that Aza behaves as an antifogging agent or restrainer during development under the correct conditions of low pH, it was necessary to utilize developing agents that function at low pH values.

Amidol, the dihydrochloride of 2, 4-diaminophenol,



was selected for use as the first developing agent because it will develop at the slightly acid pH. It is an aromatic, organic developing agent which is included in the Kendall classification (that is, Kendall associates developer activity with a structural group $a\text{-}(c{=}c)_n b$, where c=c represents two carbon atoms joined by a double bond, "n" is zero or an integer, and "a" and "b" may be either amino or hydroxyl groups, or substituted amino groups).

In order to have a developer which changes less rapidly in activity with change in pH, and which is widely different from the common developing agents, the ferrous ethylenediaminetetraacetate (EDTA) complex ion was selected. Developing solutions based on this complex[35] can be prepared which show little change in activity over a pH range of 3 to above 10. One possible drawback to using this developer is the possibility of a complex reaction with Aza. However, no unusual coloration appeared when Aza was placed in the Fe-EDTA solution. Aza also gave a negative ferric chloride test.

Amidol was used to process 5302 Film, (chosen for its repeatability and probable lack of addenda). The Fe-EDTA complex was used to process both the 5302 and 5060 Films, (chosen as a representative modern camera film).

Each developer-film-pH combination was tested in the presence and the absence of Aza and KBr, (chosen as a reference because of its common use as an antifogging agent in developing solutions). This procedure sensitometrically generated 3 characteristic curves:

1. Control - developer in the absence of both Aza and KBr.
2. Aza - Control in the presence of Aza;
3. KBr - Control in the presence of KBr.

Each set of characteristic curves was subsequently evaluated qualitatively for trends in contrast index, exposure index, and fog suppression. It should be emphasized that for this work, I felt it more essential to obtain the sensitometric data on the different developer - emulsion - pH combinations rather than to make any attempt to specify more exactly or quantitatively for any particular given set of conditions. The sample size, n, for the number of replicates was limited to 2 or 3 simply because of the time factor involved. This did not hinder the qualitative interpretation of the sensitometric data.

To test the possibility of Aza being more concentrated and therefore more extensively adsorbed on the emulsion grains after drying, the property of Aza of deaggregating or displacing adsorbed 1,1'-diethyl-2,2'-cyanine iodide dye from a silver bromide emulsion was utilized[31,33].

As previously described, the strength of the J-band of the dye depends on the concentration of the dye in the emulsion. If Aza is more concentrated and more extensively adsorbed in the dry emulsion, then it should cause a greater decrease in the strength of the J-band of the dye in the dry emulsion than when still wet.

In the sensitometric evaluation of Section 1 of this work, the nitrogen burst apparatus was selected as the method of processing. The apparatus is described in detail in the M.S. thesis of Barry Britton, R.I.T. 1972. One reason, in particular, for selecting the nitrogen burst is the susceptibility of both Amidol and Fe-EDTA developers to aerial oxidation. All solutions were deaerated with nitrogen before, during, and after mixing freshly before each run to minimize this oxidation. The susceptibility of the ferrous complex to aerial oxidation increases with pH over the range, 3 to 10, although the solutions are stable in the absence of oxygen.[36]

Processing temperature was maintained at a constant 24 ± 0.5C in every case. The temperature was recorded before and after each processing run and in no case did it fall outside of the ±0.5C limits.

Processing time was varied according to developer-film-pH combination. Initially four development times per run were used, and this was later reduced to three which was found to be adequate for this work.

All chemicals were weighed on the Mettler H10 Analytical Balance for an accuracy of ±0.1 mg, and the Beckman research pH meter was used and checked against standard NBS buffer solutions in the vicinity of the required pH, (accuracy limited by NBS buffer, and usually ±0.02 pH). All sensitometric strips were exposed on a KODAK Process Control Sensitometer Model 101.

For each set of replicates, the compartment orientation and the dense end up or down orientation of each individual strip was changed to reduce any compartmental or directional effects of the nitrogen burst apparatus.

The developed densities were then read on the MacBeth Transmission Densitometer Model TD-102 with a repeatability of ±0.01 density units.

This process gave very good repeatability. Depending, of course, on the developer-film-pH combination and the level of exposure, ±2 sigma were observed from near ±0.01, (at the base plus fog level), to near ±0.10 at some of the higher densities.

Section 2 of this work involves the cyanine-dye displacement study by Aza in the wet versus the dry silver-bromide emulsion. A negative fine-grain silver-bromide emulsion was prepared for this analysis. The same concentration of dye, (0.15g/mole Ag Br), was used for each analysis in the presence and the absence of Aza both wet and dry. All emulsions were hand coated on the substrate side of 5-inch by 7-inch clear cellulose-acetate sheets with a hand coating knife set at 0.009-inch clearance. Each coating for the required set of conditions was scanned on the Beckman DK-2A Spectrophotometer in the Graphic Arts department at R.I.T. from 380 to 730 nm. This particular instrument utilizes an integrating sphere, IX photomultiplier, a barium sulfate reference or blank, and monochromatic illumination of the sample. Both reflection and transmission spectra were run for each sample in the total transmission operating mode so that absorbance values for wavelengths of particular interest could be calculated where:

percent Absorption=100-(percent Transmission + percent Reflection). Before each scan, the transmittance scale of the instrument was calibrated for every wavelength between 380 and 730 nm, by using no sample and two barium-sulfate reflectors, one placed in the sample beam and the other placed in the reference beam. The following is a list of instrument scale settings maintained at the specified values throughout the entire course of this investigation:

1. Time constant = 0.2;
2. Range = D - 100-percent;
3. Sensitivity = 0.12;
4. Scanning time = 90mm/min.;
5. Abscissa Scale = 10mm/cm.

The data of primary interest for this evaluation were the strengths of the J-bands under the following test conditions:

1. cyanine dye in the absence of Aza wet;
2. dye in the presence of Aza wet;
3. the two preceding conditions after drying.

Through many unsuccessful runs, a procedure was finally perfected which would yield J-band absorbance values to within ±1.0 percent. This procedure is described in detail in Section 2 of the text. The concentration of Aza on drying should be increased by an order of magnitude, therefore, a major change in equilibrium was anticipated, and the sample size required to detect this change need not be large.

SECTION 1

This section describes the sensitometric evaluation of the restraining and antifogging properties of Aza and KBr in development.

pH Study of 5302 Film Processed in Amidol

Experimental Procedure. The Amidol developing solution was used at pH values of 6, 7, and 8.

The developing solutions were prepared as follows:

1. 800 ml distilled water was deaerated with nitrogen gas using a fine-fritted-glass gas-bubbling apparatus.

2. 5 grams EASTMAN Practical Grade Amidol, (catalog number P-614), and 75 grams sodium sulfite, (Baker Analyzed Reagent), were dissolved in the water in a 1 liter beaker while nitrogen gas was bubbled through the solution.

3. the pH of the solution was adjusted with acetic acid or sodium hydroxide.

4. the solution was then transferred to a 1 liter volumetric flask and adjusted to 1 liter with deaerated distilled water of the same pH.

5. a small portion of the final solution was then checked for the correct pH.

6. Aza and KBr, when needed, were added at 8.4×10^{-3} m/l after the Amidol and sulfite prior to pH adjustment. The KBr used was Baker Analyzed Reagent.

A sample of Aza known to be satisfactory as an emulsion stabilizer was obtained, (in the form of the sodium salt), by Dr. Carroll from Eastman Kodak Company. Because the amount was limited, additional Aza was acquired from the Aldrich Co., (catalog number S 37352-4). The Aldrich Aza was compared to the Kodak Aza, (as a reference), by mixed melting points and potentiometric titrations with silver nitrate. The samples were equivalent in these tests, which are described in Appendix A.

7. each solution was prepared immediately prior to use to minimize aerial oxidation.

8. the temperature of the solution was adjusted to 24 ± 0.5 C.

The 5302 Film, (emulsion number 183-531), was exposed by the KODAK Process Control Sensitometer Model 101, (serial number 856; lamp number 2419), with a net exposure of 54 m.c.s. through a previously calibrated Kodak step wedge and a 0.80 N.D. filter. No safelight was used during development. The nitrogen burst apparatus was used for processing with burst durations of 1.2 seconds every 8 seconds. Development times were 2, 4, and 6 minutes. After development, each sensitometric strip was stopped for 30 seconds in a 14-percent solution of acetic acid. The high concentration of acid in the stop bath was necessary because Amidol continued to develop in conventionally dilute stop baths. The strips were then fixed for 2 minutes in F-5 fixer, washed 5 minutes with water, and dried.

All density versus log exposure curves from these sensitometric strips were plotted in the following manner:

1. the density values for each replicate of each of the eleven exposure levels were averaged, and the average values were plotted with ±2 sigma limits.

2. the curve of best fit was then drawn between the average values within the specified limits. This method was selected so that long tables of density readings could be eliminated from the Appendix.

Regression analysis was not profitable because of the small sample size. Contrast and exposure index versus time curves were plotted by connecting mean values with straight lines to indicate trends.

Contrast index was measured as follows[37]:

1. a point was selected on the characteristic curve where the density was 0.10 above base plus fog density. This was called the minimum density point.

2. with this point as a center, an arc was drawn with its radius equal to a distance of 2.0 on the log E scale. The intersection of this arc and the characteristic curve was called the maximum density point.

3. the slope of a straight line drawn between these two points was the contrast index.

Exposure index, a measure of film speed, was calculated as follows:

1. the minimum density point was selected as above.

2. a vertical line was drawn from this point to intersect the log E scale. The antilog of the exposure value at the point of intersection was taken and designated as E.

3. the exposure index was then calculated from the following formula:

$$\text{Exposure Index} = \frac{0.80}{E} .$$

Results: Figures 1 through 4 show the effects of Aza and KBr at a pH of 6.0

For each development time Aza and KBr restrained development. However, unlike KBr, Aza restrained the higher densities more than the lower ones. Both Aza and KBr showed a tendency to suppress developer fog especially for the longer development times, even though the fog level was low. Aza produced lower contrast index while KBr caused slower speed.

Figures 5 through 8 are the results at a pH of 7.0.

The preceding results show that the activity of Amidol was greater at pH 7.0 than at 6.0. The fog level in the absence of Aza and KBr was appreciable, especially at longer development times. Aza still suppressed the higher densities more than KBr, but at pH 7.0 Aza suppressed both speed and fog to the same extent as KBr.

Figures 9 through 12 show the results at pH 8.0.

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 183-531
Developer: Amidol Time: 2 min. pH: 6.0
Control: ————————
KBr: —— — ——
Aza: ————————
KBr and Aza present at 8.4 X 10^{-3} m/l.
±2 sigma shown from 3 replicates.

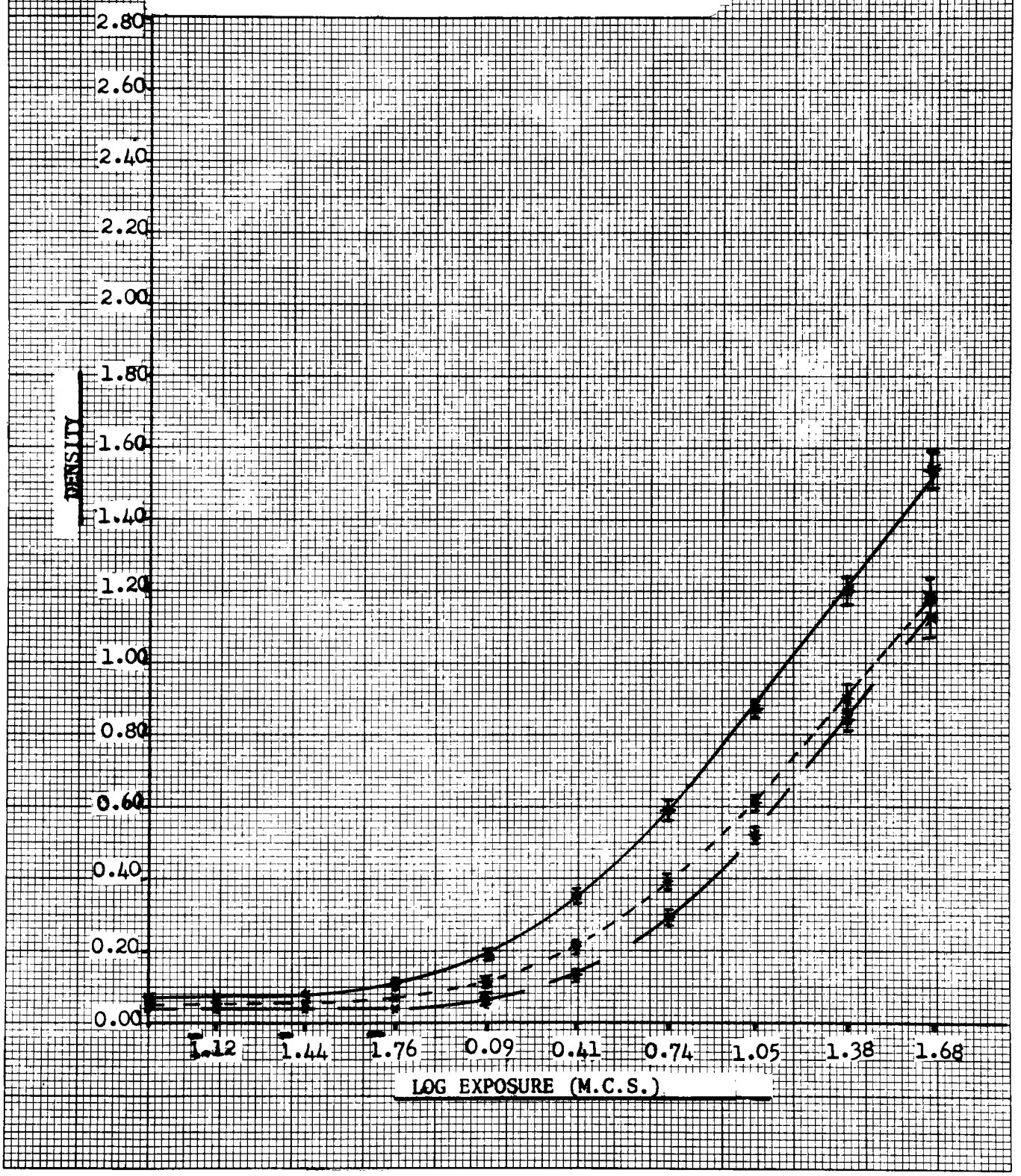


Figure 1

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 183-531
Developer: Amidol Time: 4 min. pH: 6.0
Control: ——————
KBr: —— — —
Aza: — — — —
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 3 replicates.

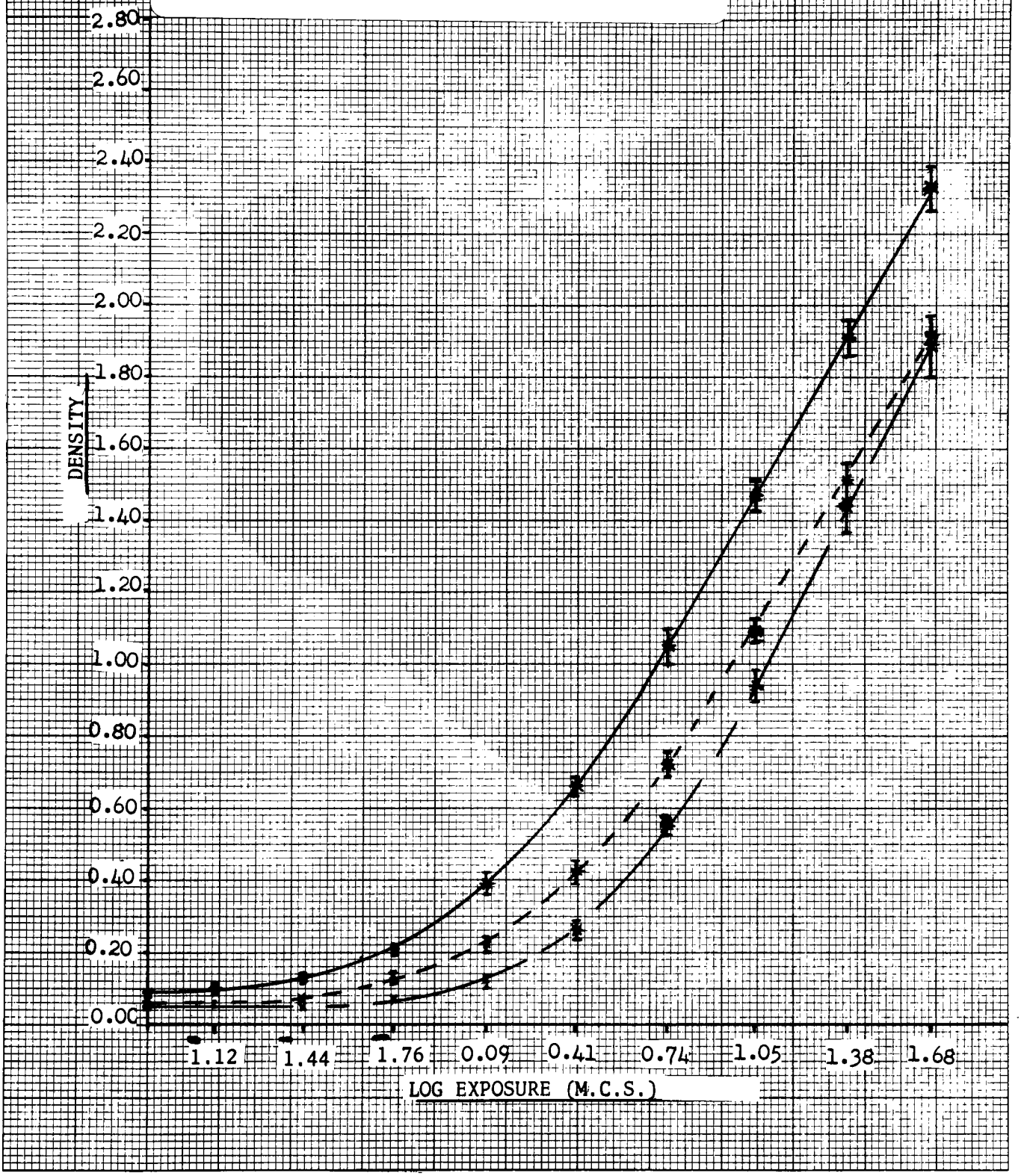


Figure 2

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 183-531
Developer: Amidol Time: 6 min. pH: 6.0
Control: ————————
KBr: ———— — ————
Aza: ————————
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown fron 3 replicates.

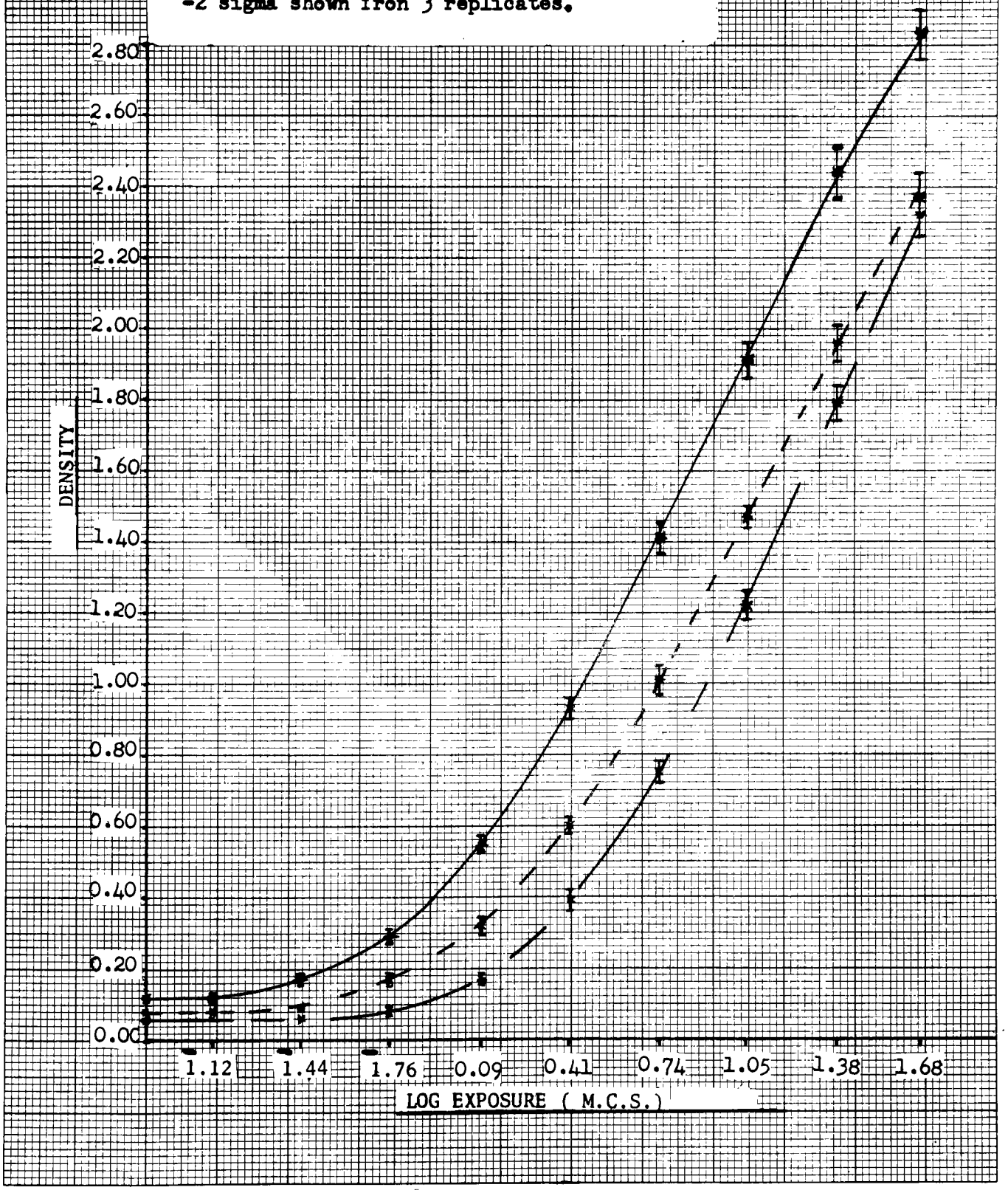


Figure 3

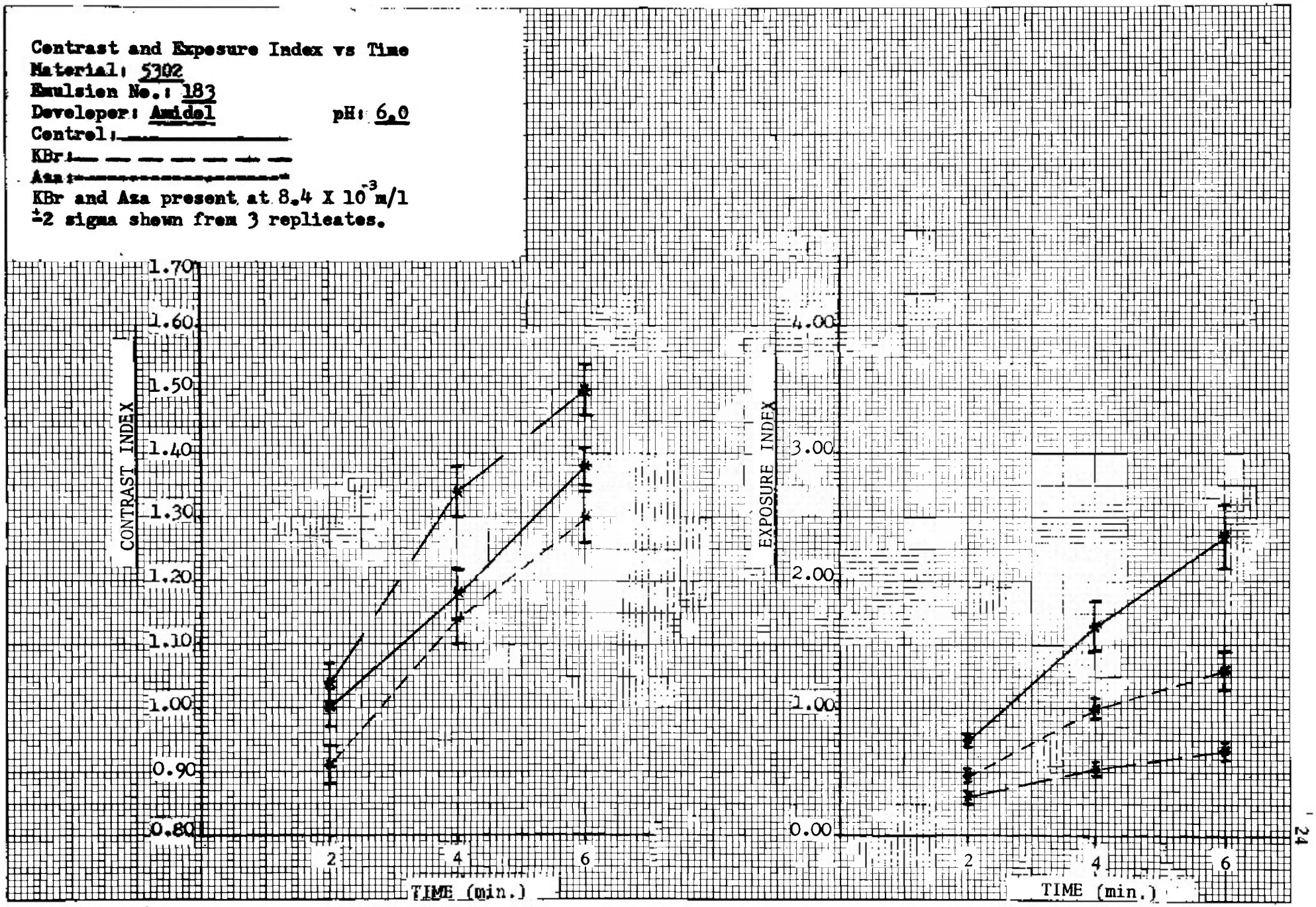

Contrast and Exposure Index vs Time
Material: 5302
Emulsion No.: 183
Developer: Amidol pH: 6.0
Control:
KBr:
Aza:
KBr and Aza present at 8.4 X 10^-3 m/l
±2 sigma shown from 3 replicates.
CONTRAST INDEX
1.70
1.60
1.50
1.40
1.30
1.20
1.10
1.00
0.90
0.80
EXPOSURE INDEX
4.00
3.00
2.00
1.00
0.00
2
4
6
TIME (min.)
TIME (min.)

Figure 4

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 183-531
Developer: Amidol Time: 2 min. pH: 7.0
Control: ————————
Aza: - - - - - - - - - - -
KBr: — — — — —
KBr and Aza present at 8.4 X 10^{-3} m/l.
±2 sigma shown from 3 replicates.

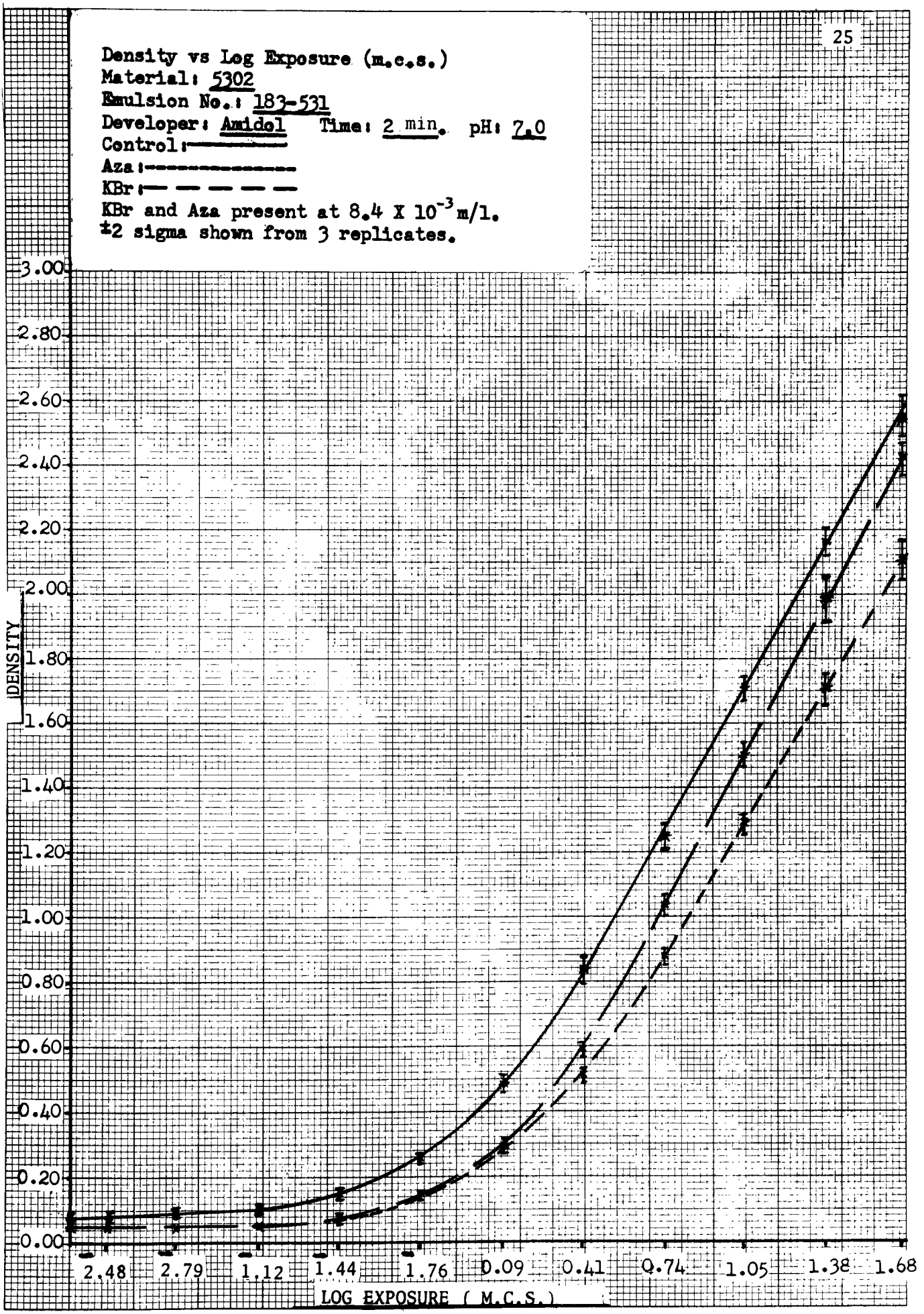


Figure 5

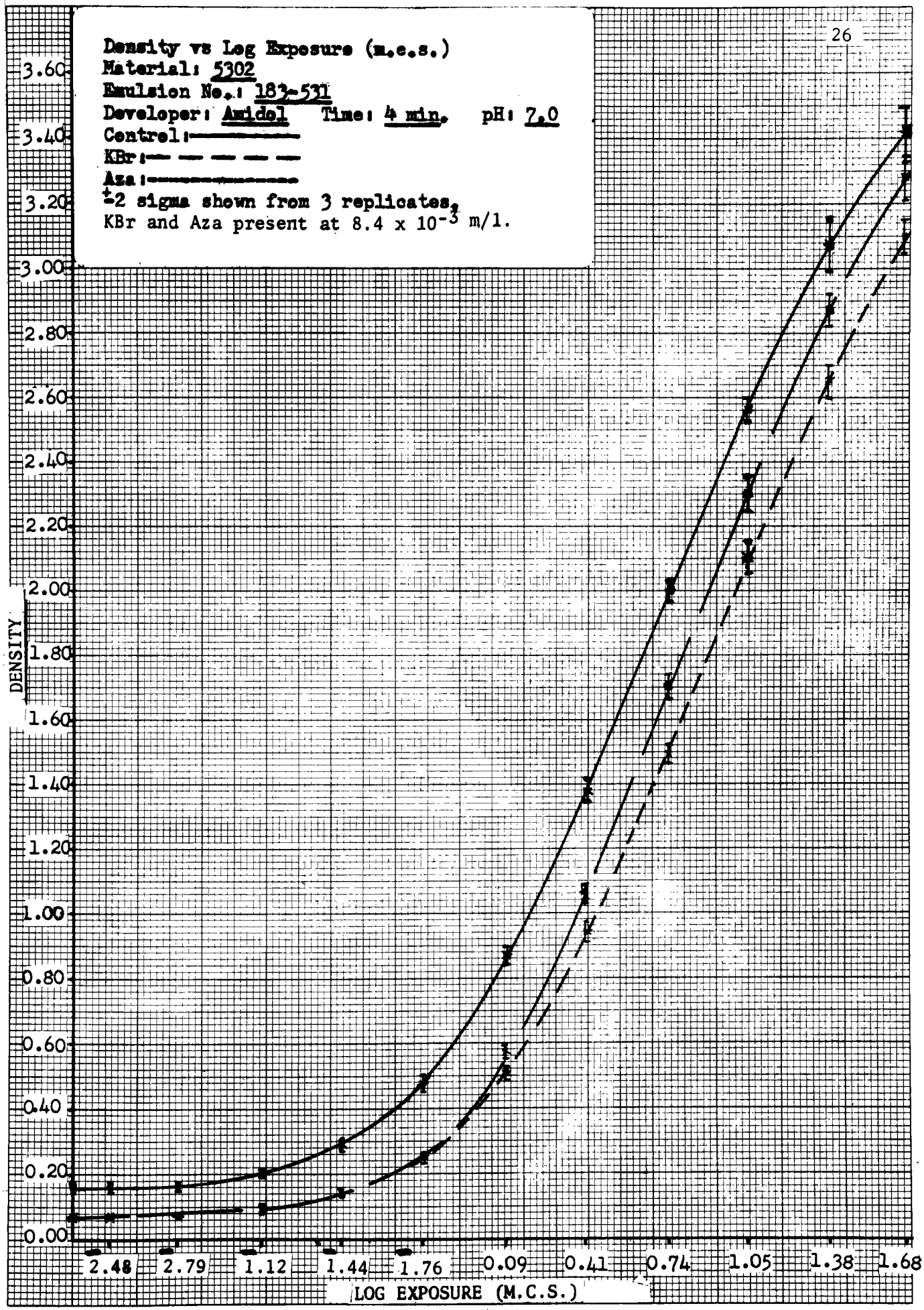

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 183-531
Developer: Amidol Time: 4 min. pH: 7.0
Control:
KBr:
Aza:
±2 sigma shown from 3 replicates.
KBr and Aza present at 8.4 x 10-3 m/l.
DENSITY
3.60
3.40
3.20
3.00
2.80
2.60
2.40
2.20
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
2.48
2.79
1.12
1.44
1.76
0.09
0.41
0.74
1.05
1.38
1.68
LOG EXPOSURE (M.C.S.)

Figure 6

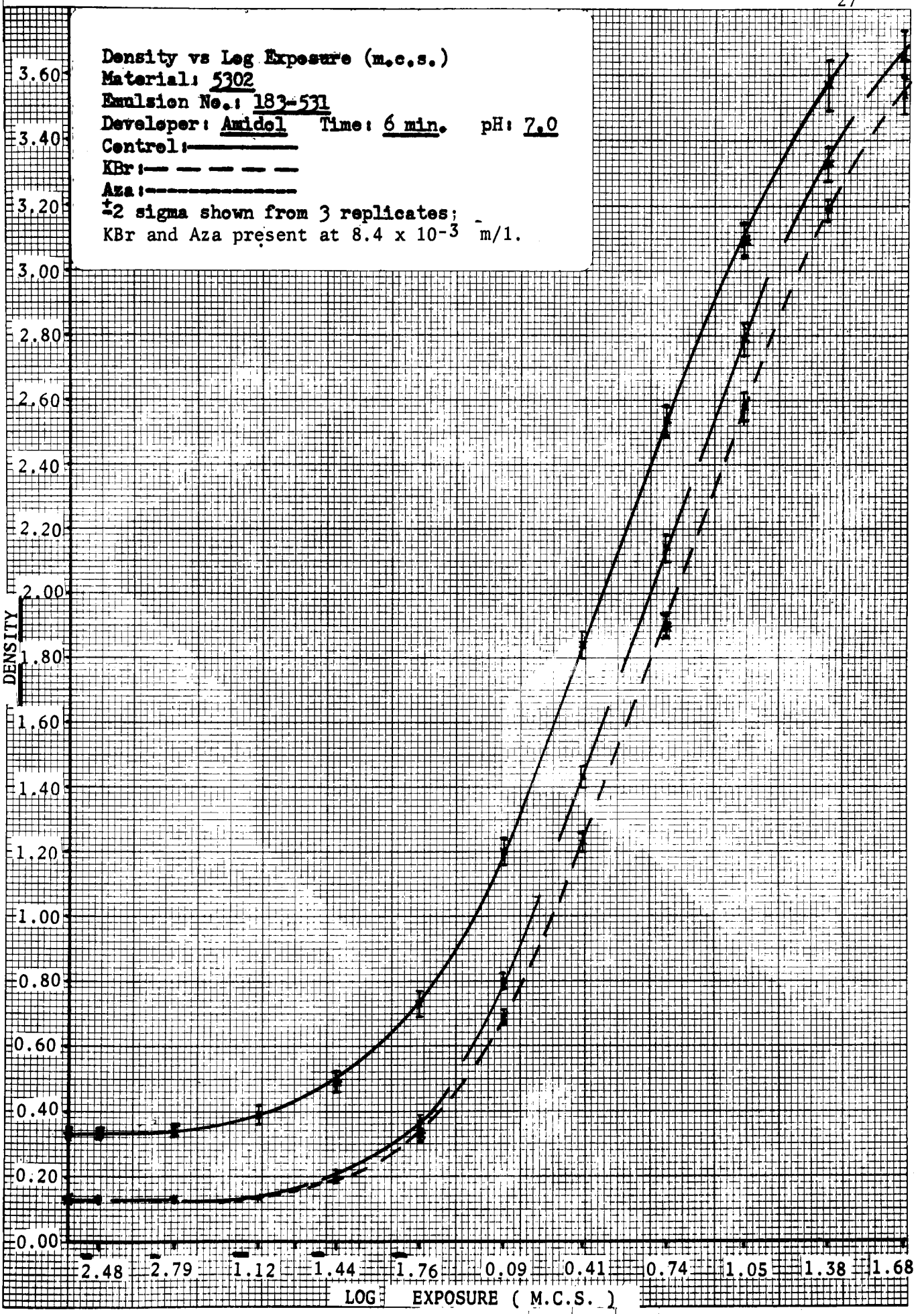

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 183-531
Developer: Amidol Time: 6 min. pH: 7.0
Control:
KBr:
Aza:
±2 sigma shown from 3 replicates;
KBr and Aza present at 8.4 x 10-3 m/1.
DENSITY
3.60
3.40
3.20
3.00
2.80
2.60
2.40
2.20
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
2.48
2.79
1.12
1.44
1.76
0.09
0.41
0.74
1.05
1.38
1.68
LOG EXPOSURE (M.C.S.)

Figure 7

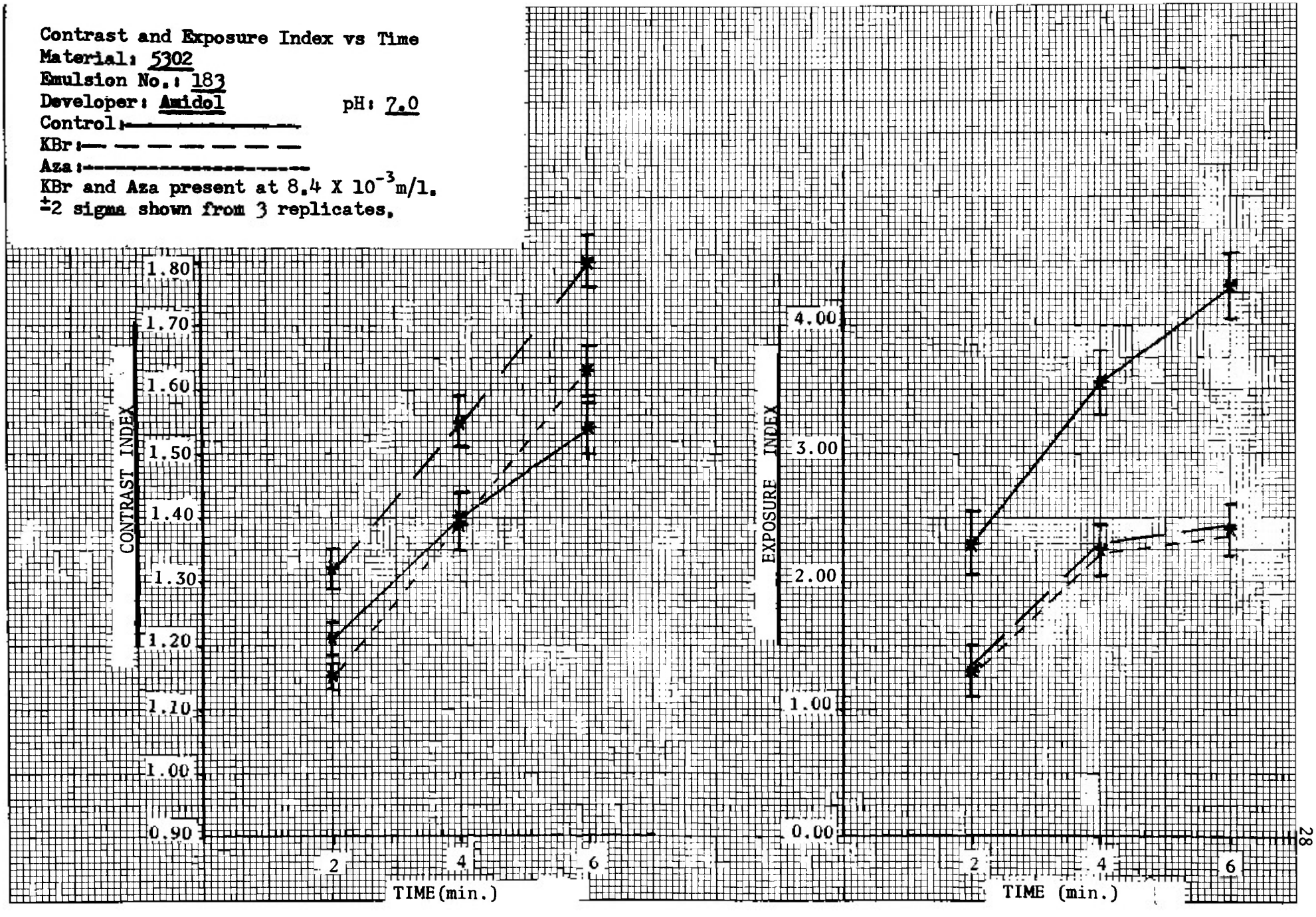

Contrast and Exposure Index vs Time
Material: 5302
Emulsion No.: 183
Developer: Amidol pH: 7.0
Control:
KBr:
Aza:
KBr and Aza present at 8.4 X 10^-3 m/l.
±2 sigma shown from 3 replicates.
CONTRAST INDEX
1.80
1.70
1.60
1.50
1.40
1.30
1.20
1.10
1.00
0.90
2
4
6
TIME(min.)
EXPOSURE INDEX
4.00
3.00
2.00
1.00
0.00
2
4
6
TIME (min.)

Figure 8

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 183-531
Developer: Amidol Time: 2 min. pH: 8.0
Control: ————————
KBr: — — — — —
Aza: ————————
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 3 replicates.

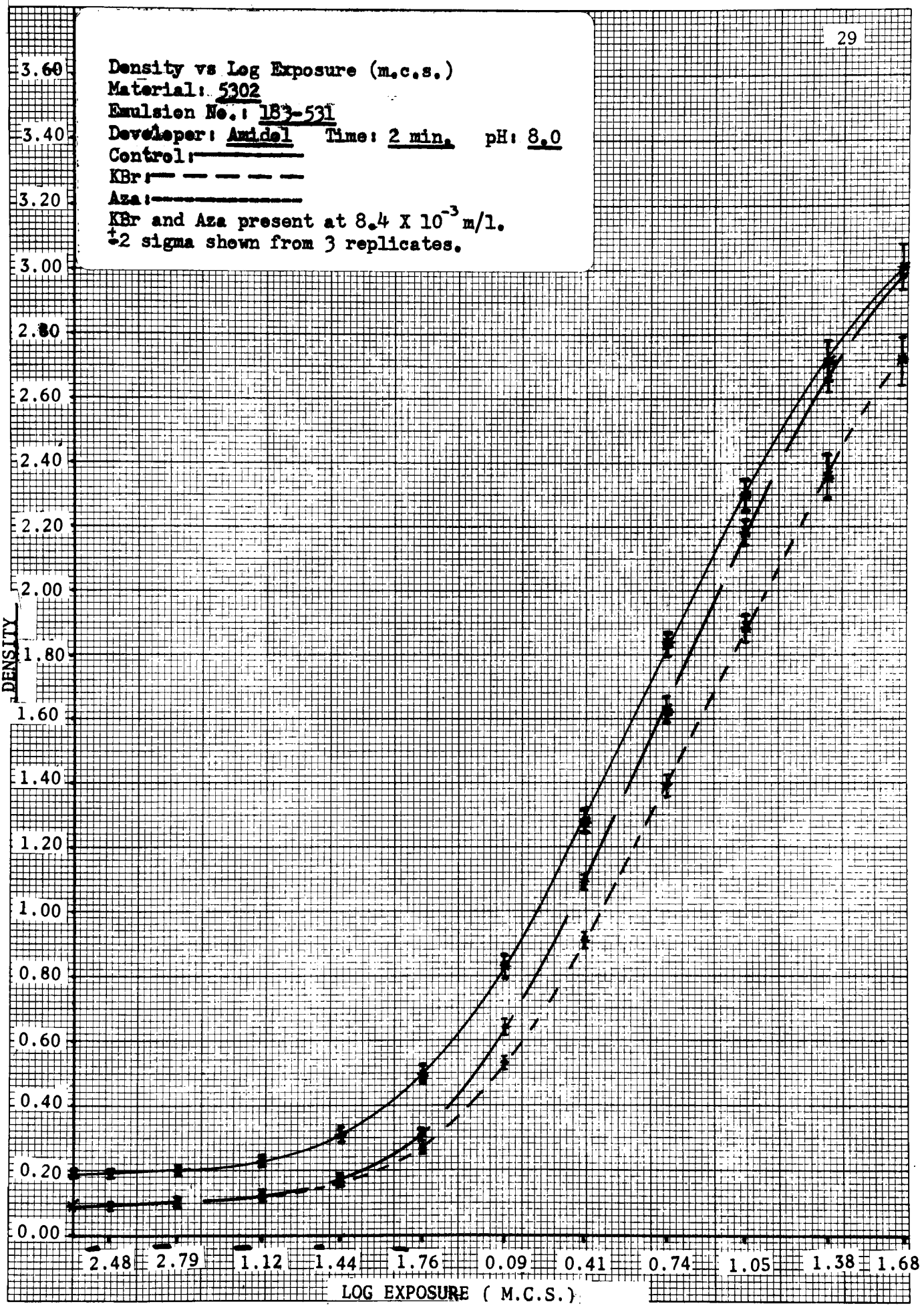


Figure 9

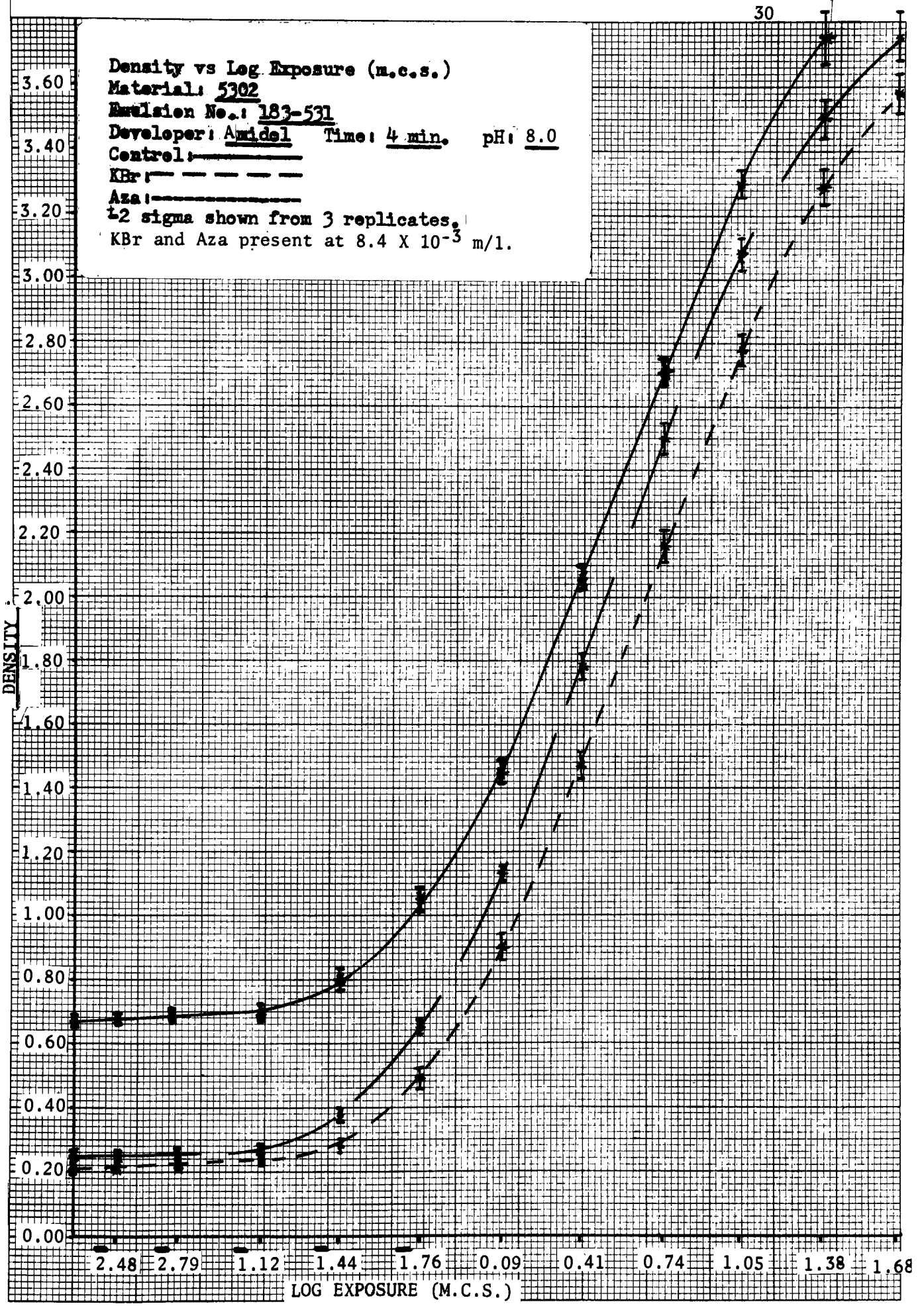

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 183-531
Developer: Amidol Time: 4 min. pH: 8.0
Control:
KBr:
Aza:
±2 sigma shown from 3 replicates.
KBr and Aza present at 8.4 X 10-3 m/1.
30
3.60
3.40
3.20
3.00
2.80
2.60
2.40
2.20
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
DENSITY
2.48
2.79
1.12
1.44
1.76
0.09
0.41
0.74
1.05
1.38
1.68
LOG EXPOSURE (M.C.S.)

Figure 10

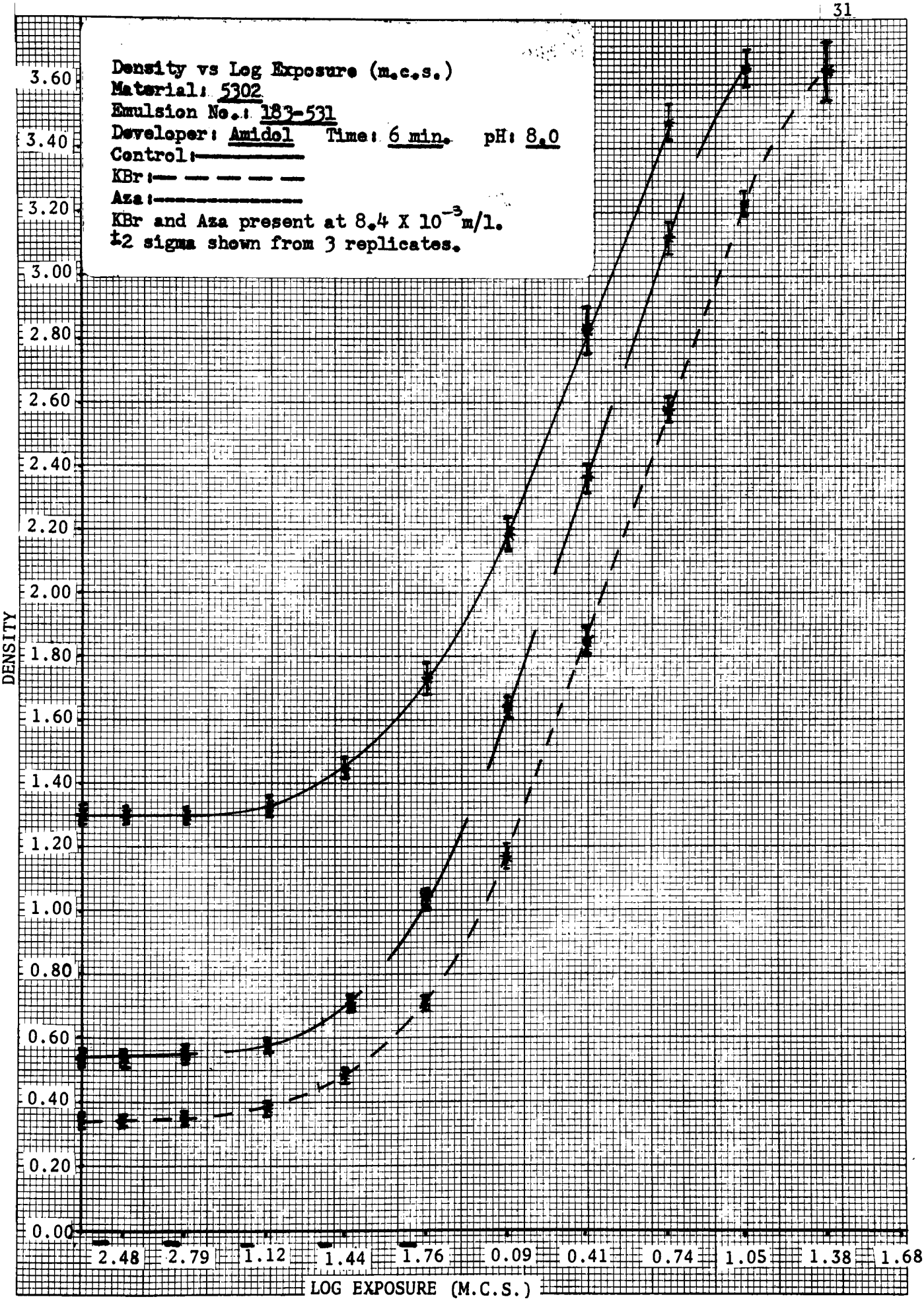

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 183-531
Developer: Amidol Time: 6 min. pH: 8.0
Control:
KBr:
Aza:
KBr and Aza present at 8.4 X 10⁻³ m/l.
±2 sigma shown from 3 replicates.
DENSITY
3.60
3.40
3.20
3.00
2.80
2.60
2.40
2.20
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
2.48
2.79
1.12
1.44
1.76
0.09
0.41
0.74
1.05
1.38
1.68
LOG EXPOSURE (M.C.S.)

Figure 11

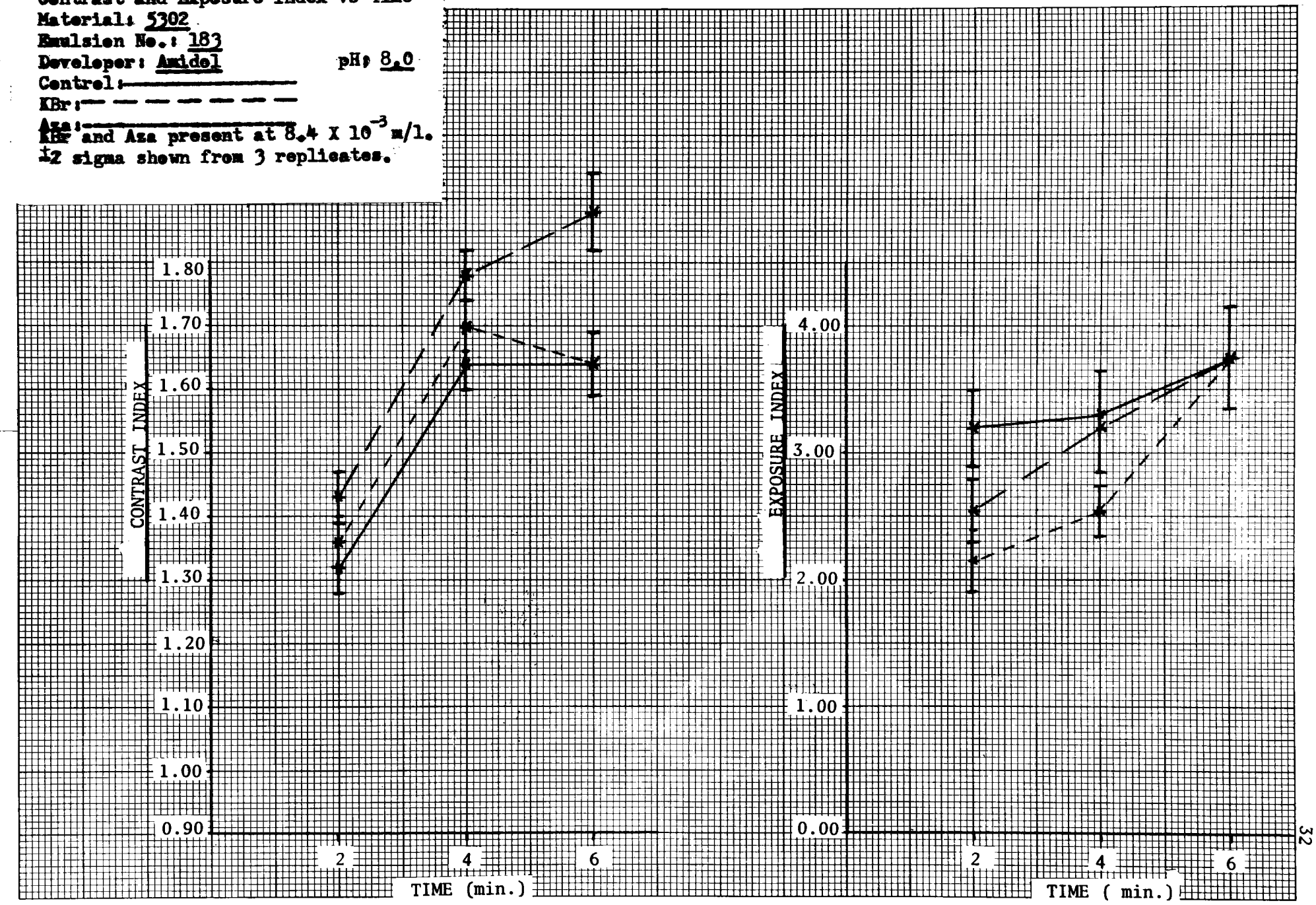

Contrast and Exposure Index vs Time
Material: 5302
Emulsion No.: 183
Developer: Amidol pH: 8.0
Control:
KBr:
Aza:
KBr and Aza present at 8.4 X 10⁻³ m/l.
±2 sigma shown from 3 replicates.
CONTRAST INDEX
1.80
1.70
1.60
1.50
1.40
1.30
1.20
1.10
1.00
0.90
2
4
6
TIME (min.)
EXPOSURE INDEX
4.00
3.00
2.00
1.00
0.00
2
4
6
TIME (min.)

Figure 12

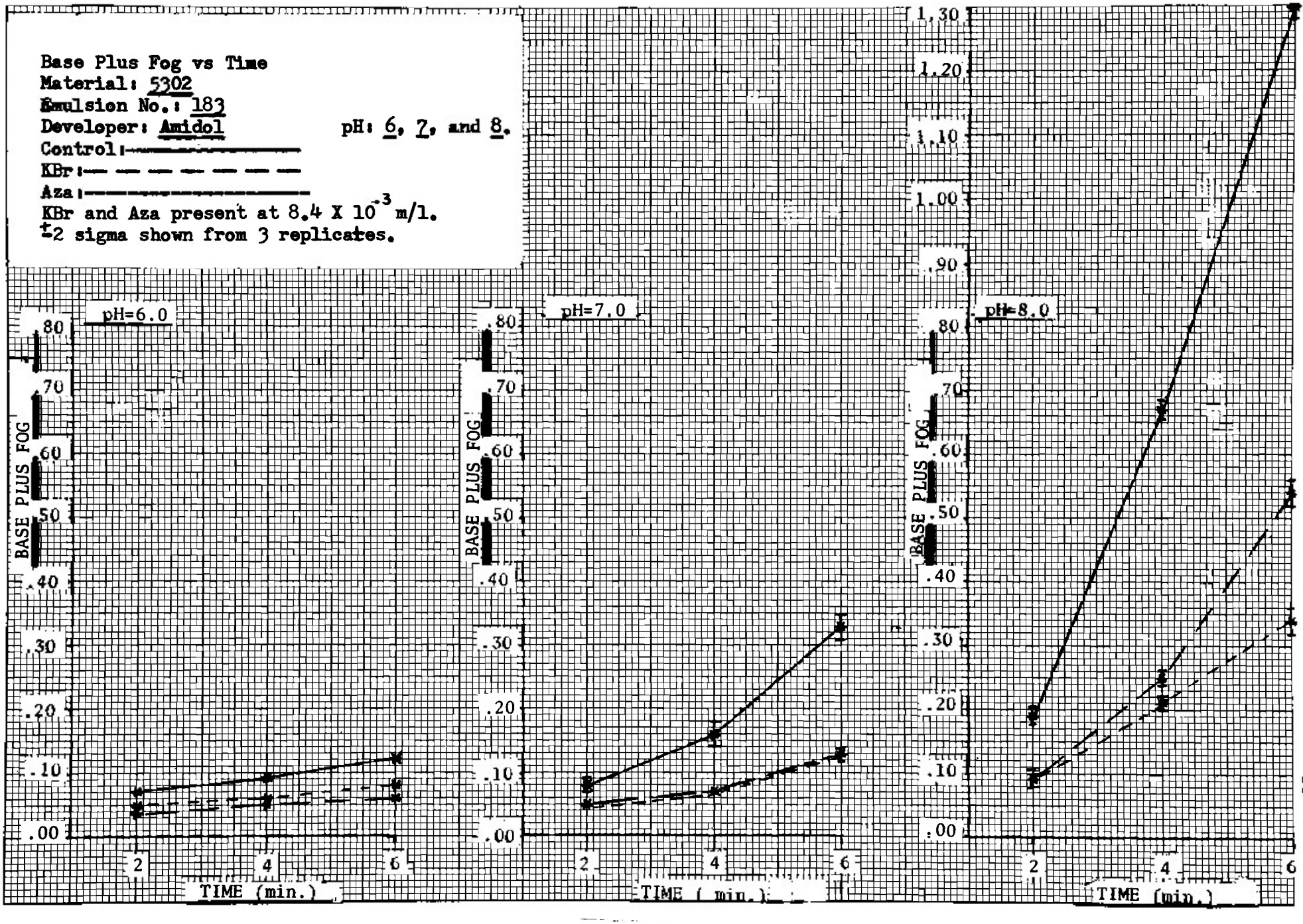

Base Plus Fog vs Time
Material: 5302
Emulsion No.: 183
Developer: Amidol
pH: 6, 7, and 8.
Control:
KBr:
Aza:
KBr and Aza present at 8.4 X 10^-3 m/l.
±2 sigma shown from 3 replicates.
pH=6.0
pH=7.0
pH=8.0
BASE PLUS FOG
TIME (min.)
.00
.10
.20
.30
.40
.50
.60
.70
.80
.90
1.00
1.10
1.20
1.30
2
4
6

Figure 13

At pH 8.0 Amidol became less selective in development of the latent image, as evidenced by the high fog level. Aza still tended to suppress the higher densities more than KBr, but because Aza was more effective in suppressing fog, the contrast index at lower densities increased. At pH 8.0 Aza tended to reduce speed more than KBr.

Figure 13 shows the base plus fog versus time curves for the three pH values tested. They reiterate the evidence that Aza and KBr were active antifoggants in Amidol developer at pH values 6.0, 7.0, and 8.0.

pH Study of 5302 Film Processed in Fe-EDTA

Experimental Procedure. The pH of the Fe-EDTA developer was varied from 4.46 to 10.0. The developing solution was prepared as follows:

1. 100 grams ethylenediaminetetraacetic acid tetrasodium salt (Eastman Practical Grade) were dissolved in 490 ml distilled water, and the solution was deaerated with nitrogen.

2. 30 grams $FeSO_4.7\ H_2O$ (Baker Analyzed Reagent) were dissolved in 490 ml of a 0.002 M H_2SO_4 solution previously deaerated.

3. the two solutions were then mixed in a 1 liter beaker by slowly adding the ferrous solution to the EDTA solution while bubbling nitrogen gas continuously through the solution during the addition. Observation - as the ferrous solution was added, the color of the mixture went from clear, to yellowish, to light pink in color. The longer the developer was allowed to remain in contact with the air, the redder it became, (approaching a blood red color). This color change on exposure to air indicated a reaction of some form, therefore, the solution was used immediately after the final pH adjustment.

4. the pH of the developer solution without adjustment was near 10.5. The pH was adjusted with acetic acid, and the EDTA served as a good buffer. All pH adjustments were made while deaerating with nitrogen. However, the bubbling was ceased just prior to the final pH adjustment, because solution turbulence affected the meter reading.

5. Aza and KBr, when required, were added at 8.4×10^{-3} m/l prior to the final pH adjustment.

6. the volume of the solution was then adjusted to 1 liter with distilled deaerated water maintained at the required pH.

The emulsion number of the 5302 film used here was 176. The same processing procedures and conditions were used as before with the exceptions of development times and stop bath. For pH values 4.46, 7.0, and 10.0, times of 4, 6, 8, and 12 minutes were used. For pH 8.5, times of 4, 7, and 10 minutes were used. A regular acid stop bath was not used because, unlike most developers, the activity of Fe-EDTA is not strongly dependent on pH; and no recommended procedure for quickly stopping development by Fe-EDTA could be found in the literature. Therefore, instead of using a stop bath, each sensitometric strip was given a 30 second spray of water following development. The system was repeatable to within ±0.05 density.

Results: Figures 14 through 18 show the effects of Aza and KBr in development of pH 4.46.

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 4 min. pH: 4.46
Control: ————————
KBr: — — — — —
Aza: —·—·—·—·—·—
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

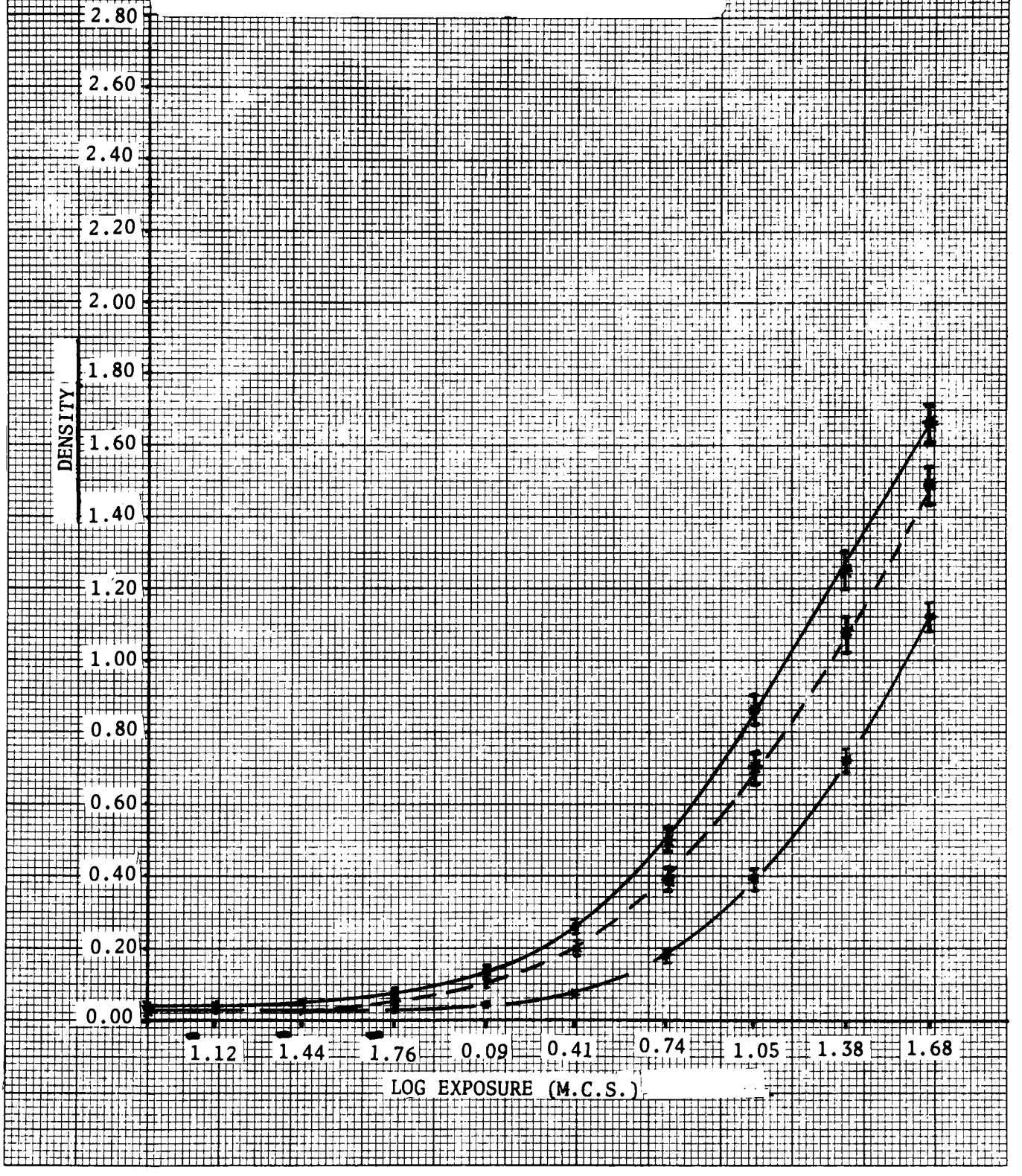


Figure 14

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 6 min. pH: 4.46
Control: ————————
KBr: — — — — —
Aza: ————————
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

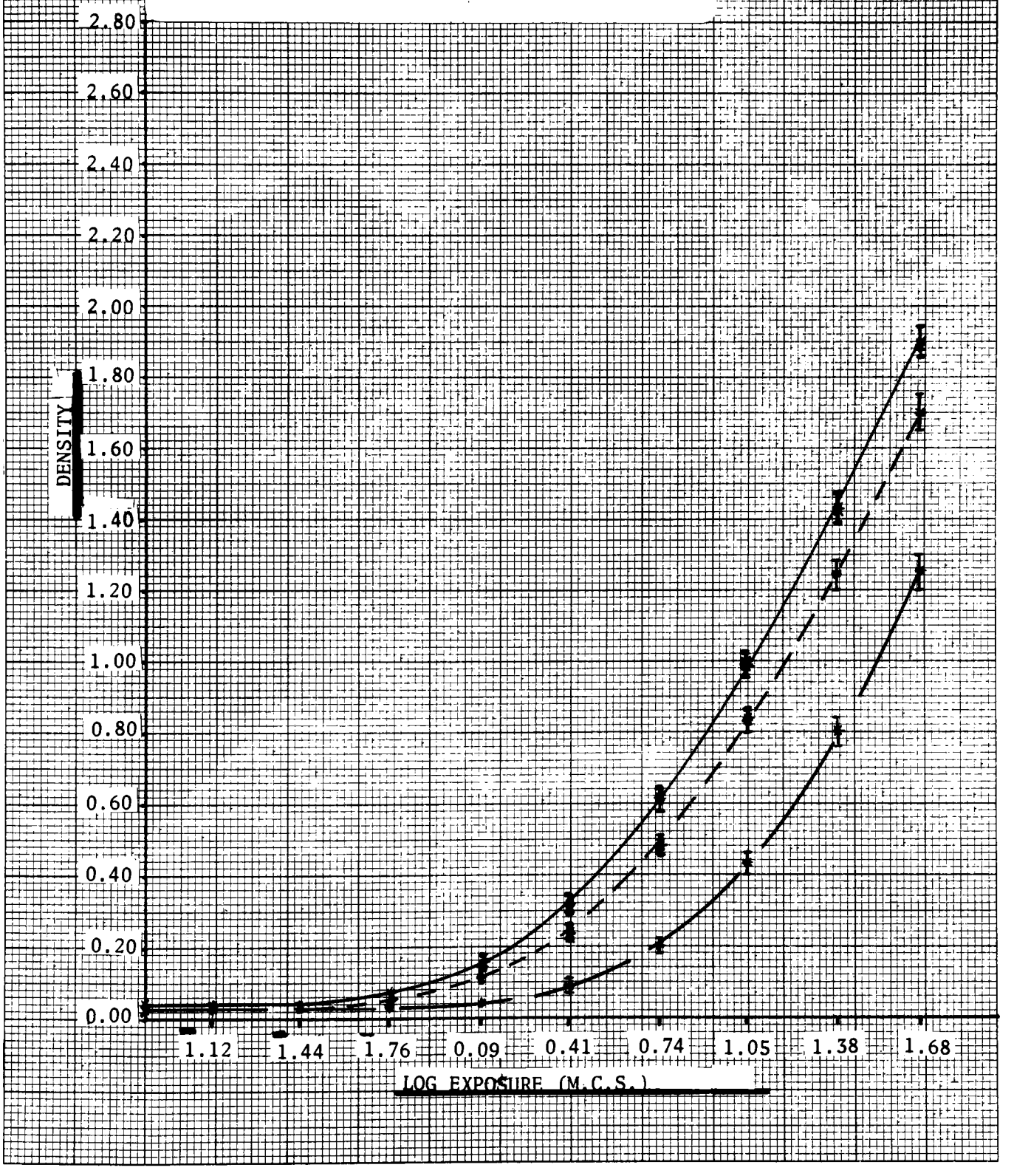


Figure 15

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 8 mkn. pH: 4.46
Control: ————
KBr: — — — — —
Aza: ————————
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

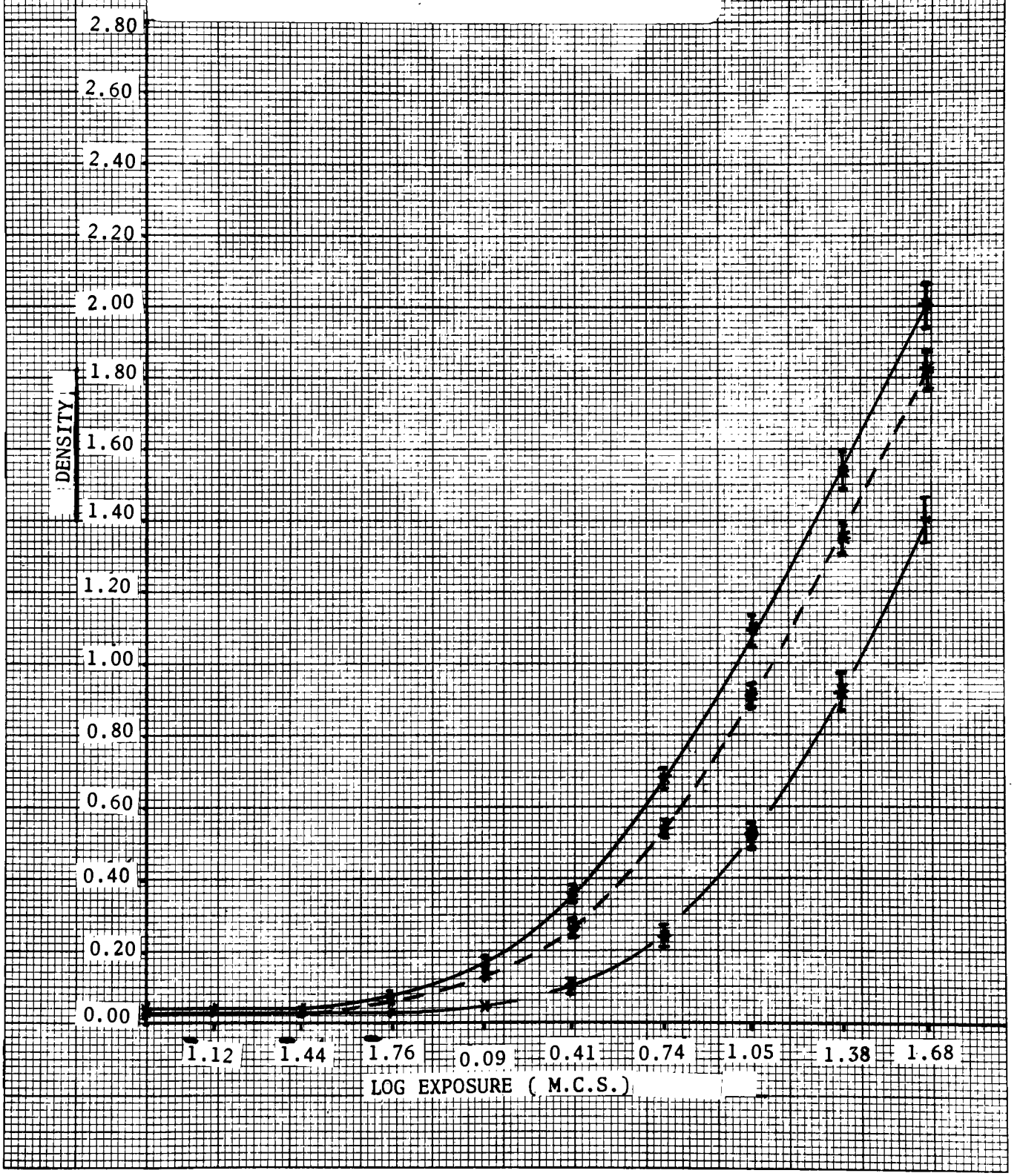


Figure 16

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 12 min. pH: 4.46
Control: ————
KBr: — — — — —
Aza: ————————
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

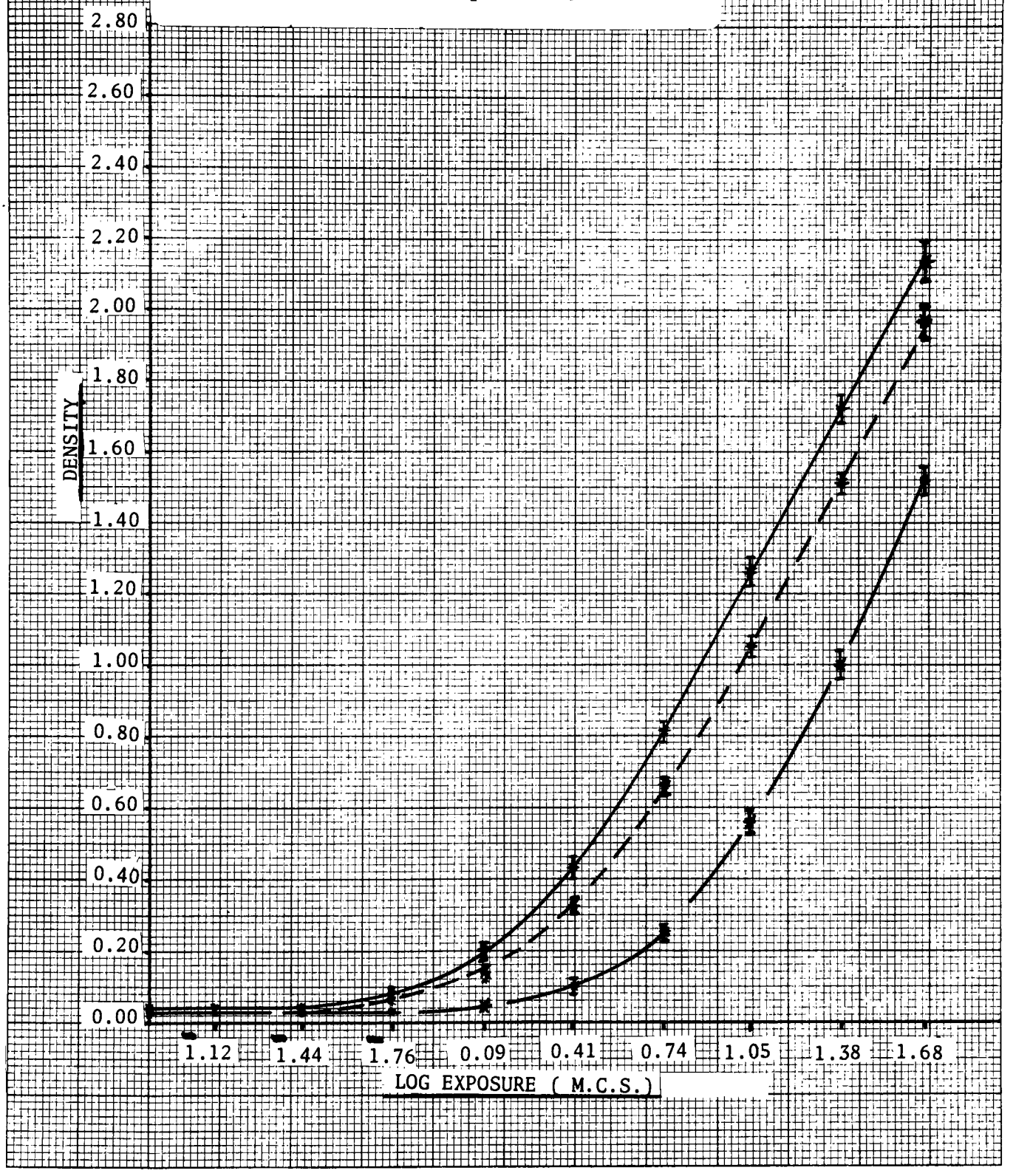


Figure 17

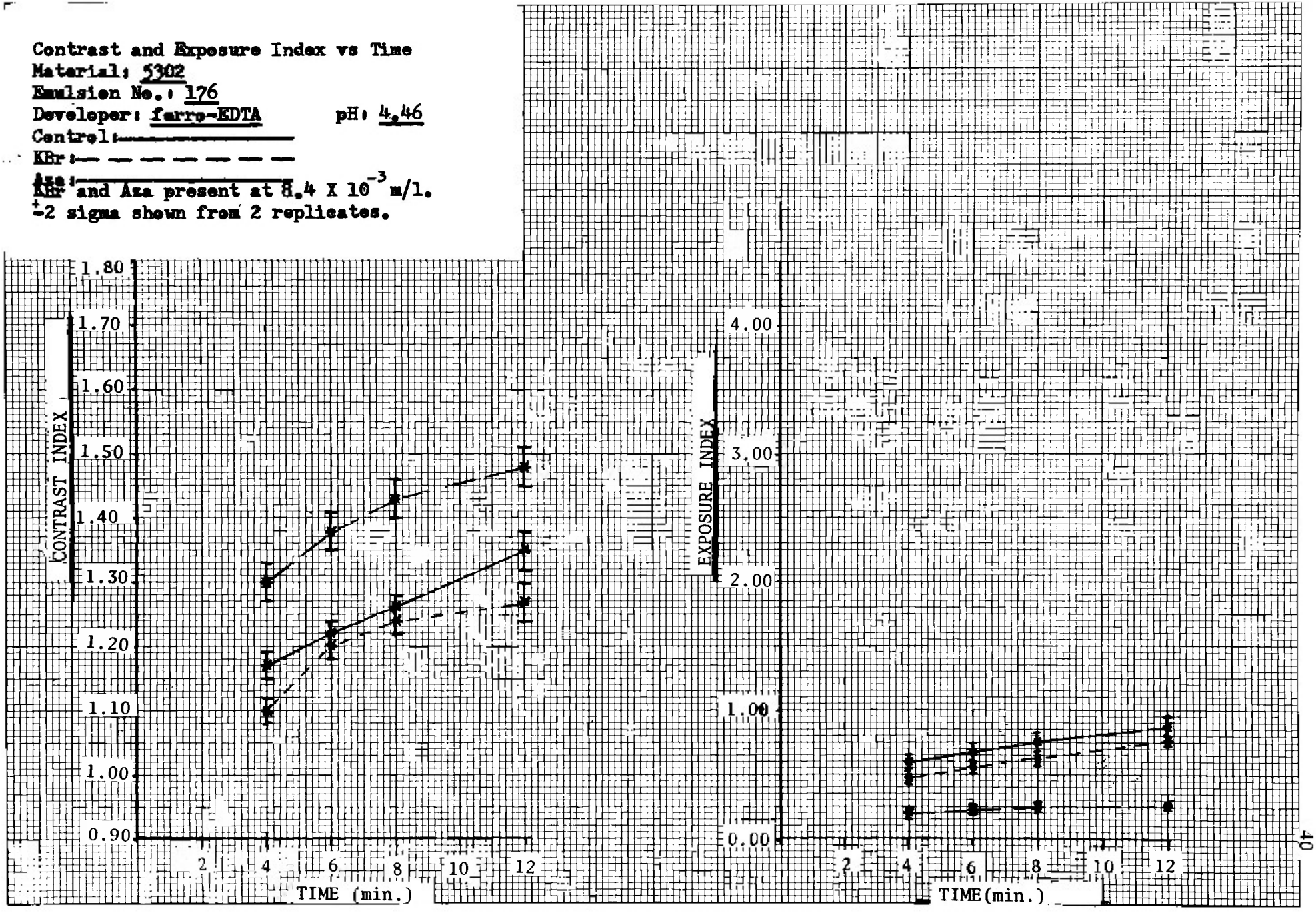

Contrast and Exposure Index vs Time
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA pH: 4.46
Control:
KBr:
Aza:
KBr and Aza present at 8.4 X 10^-3 m/l.
±2 sigma shown from 2 replicates.
CONTRAST INDEX
1.80
1.70
1.60
1.50
1.40
1.30
1.20
1.10
1.00
0.90
2
4
6
8
10
12
TIME (min.)
EXPOSURE INDEX
4.00
3.00
2.00
1.00
0.00
2
4
6
8
10
12
TIME (min.)

Figure 18

As before in the Amidol, Aza restrained the higher densities more than the lower. Aza reduced contrast index more than KBr, but KBr reduced speed more. Even at long development times the Fe-EDTA developer did not produce an appreciable amount of fog, but it is evident that Aza restrained development under these conditions.

Figures 19 through 23 show the effects of Aza and KBr under these conditions at a pH of 7.0.

At pH 7.0 the Fe-EDTA developer showed little increase in activity above that at 4.46 as expected.[35] There was still no appreciable fog for Aza and KBr to suppress, but the same trends occurred at pH 7.0 that were noted at 4.46, (i.e. Aza restrained the higher densities more, and KBr reduced speed more). However, there was less difference between Aza and KBr at 7.0. The 4 minute control had about the same gamma as the 12 minute Aza, however the latter had greater speed than the 4 minute control. This indicates that Aza did not just decrease the rate of development, and that something else was involved.

Figures 24 through 27 are the results at pH 8.5.

At pH 8.5 there was a slight increase in fog and speed compared to 7.0. Aza still suppressed higher densities more than lower while KBr increased contrast as before. Aza was not as active in restraining development at pH 8.5 as at the lower pH values, and it even tended to slightly increase the fog level.

Figures 28 through 32 show the results at pH 10.0

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 4 min. pH: 7.0
Control: ————
KBr: — — — — —
Aza: ————————
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

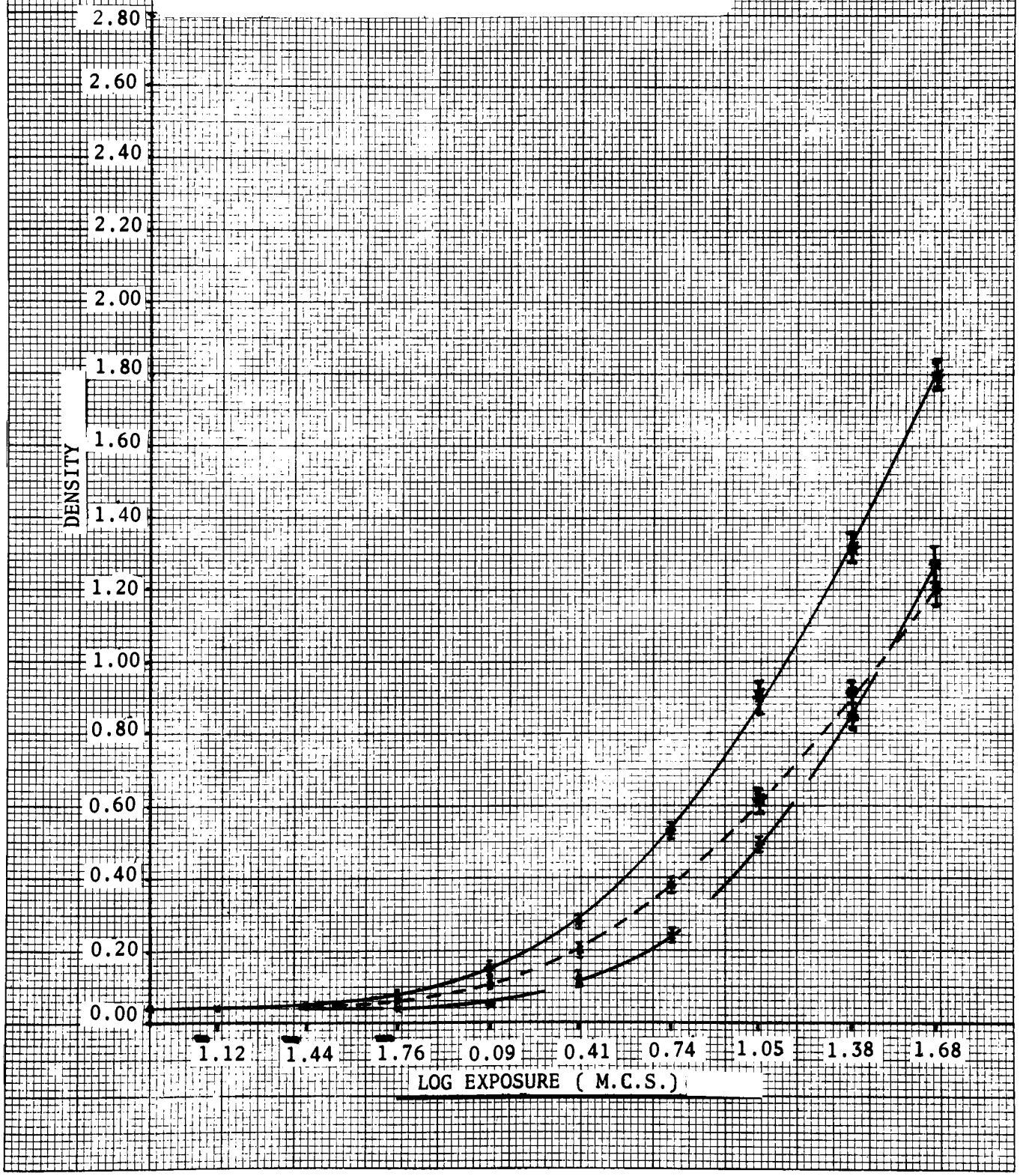


Figure 19

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 6 min. pH: 7.0
Control: ——————
KBr: — — — — —
Ass: ——————
KBr and Ass present at 8.4×10^{-3} m/l.
± 2 sigma shown from 2 replicates.

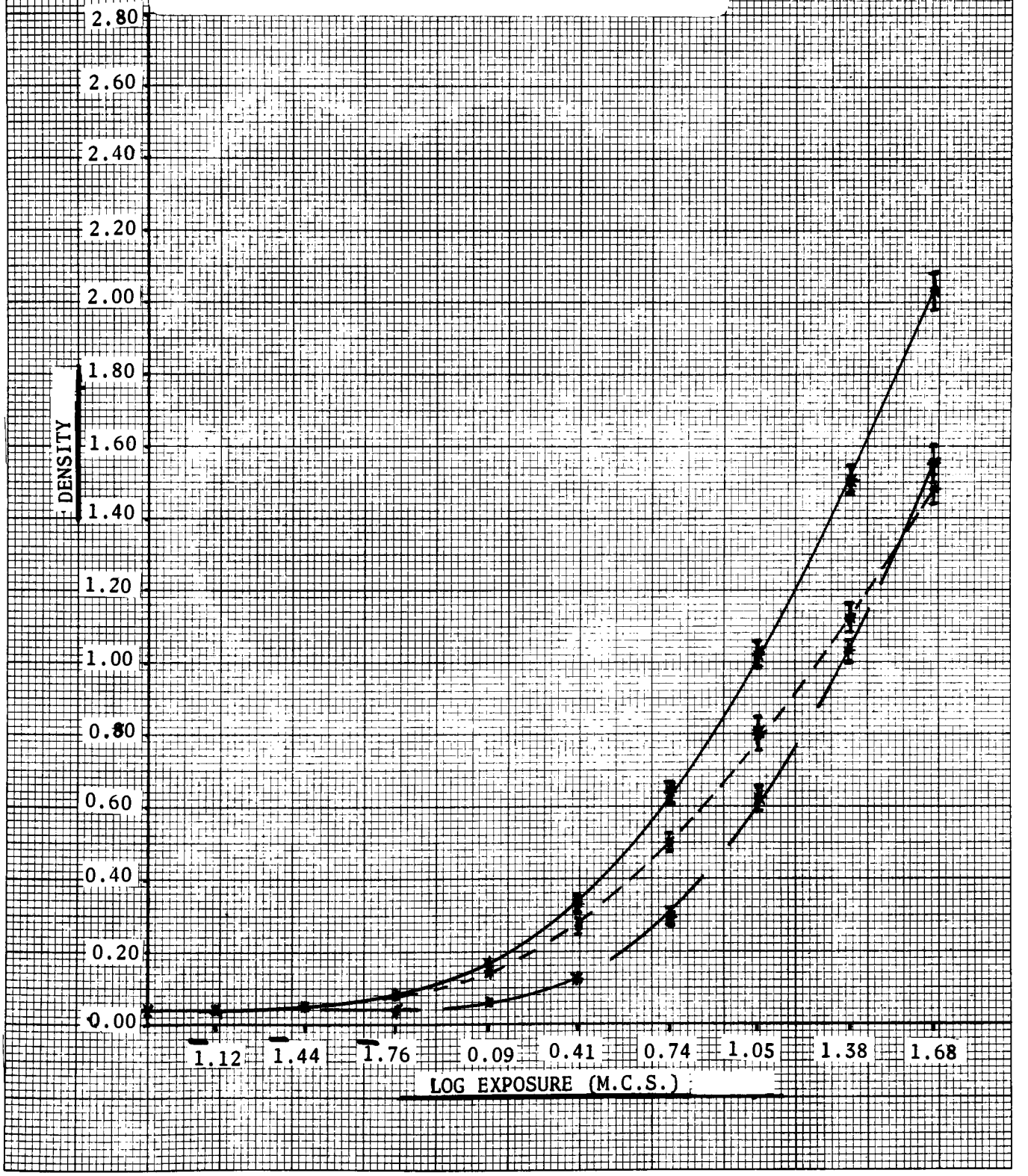


Figure 20

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 8 min. pH: 7.0
Control: ————
KBr: — — — —
Aza: ————————
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

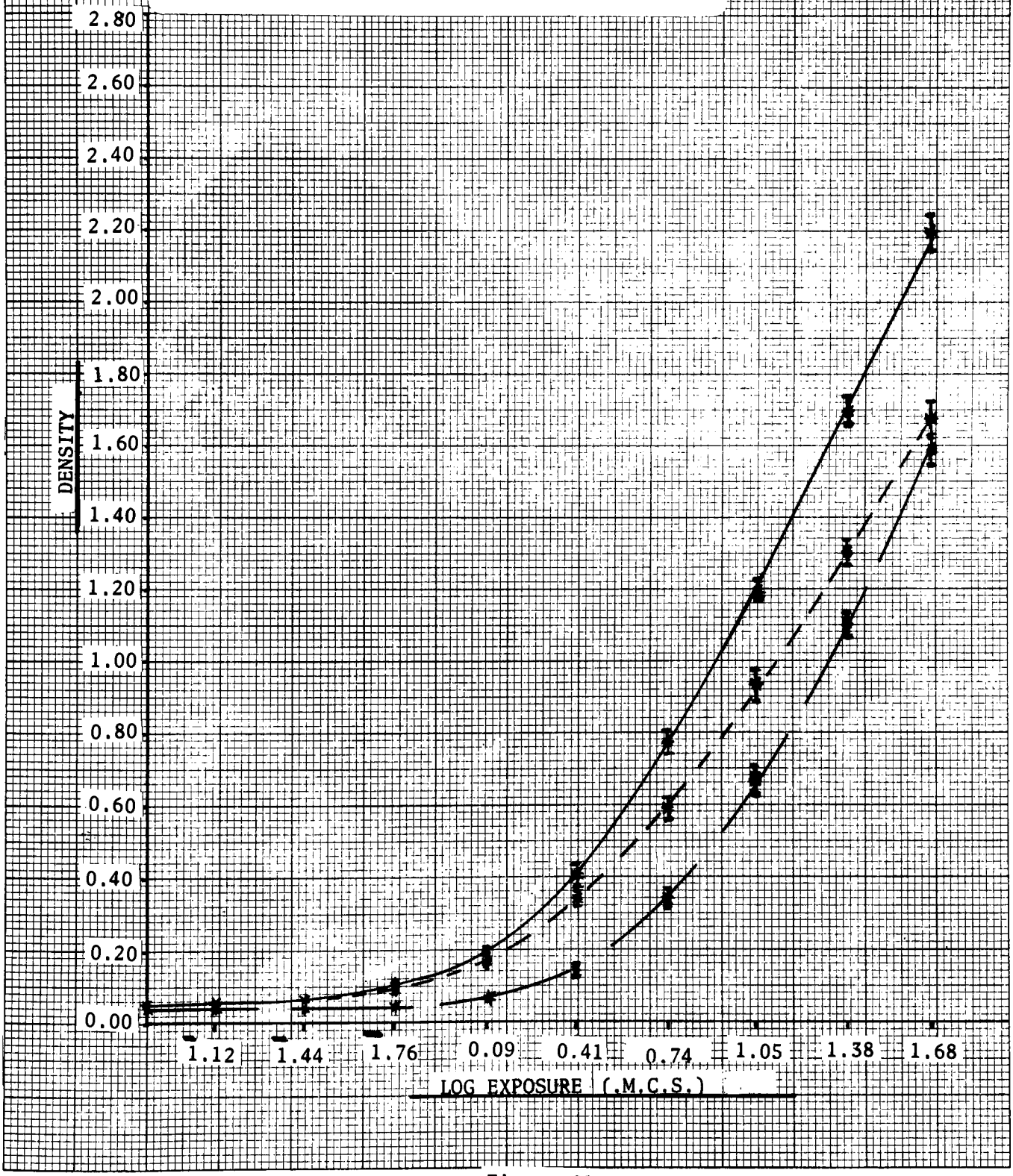


Figure 21

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: Ferro-EDTA Time: 12 min. pH: 7.0
Control: ————————
KBr: — — — — —
Aza: ————————
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

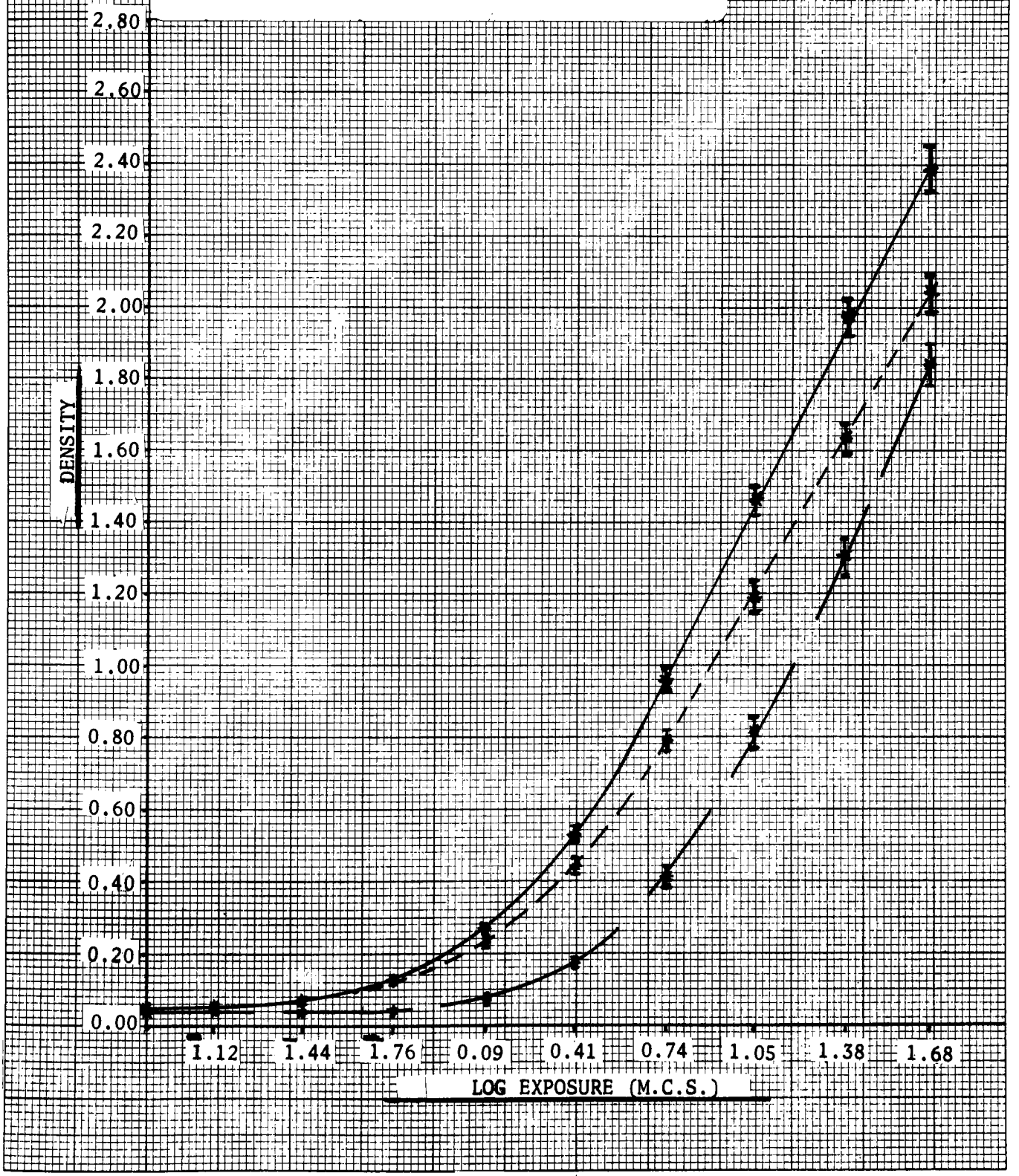


Figure 22

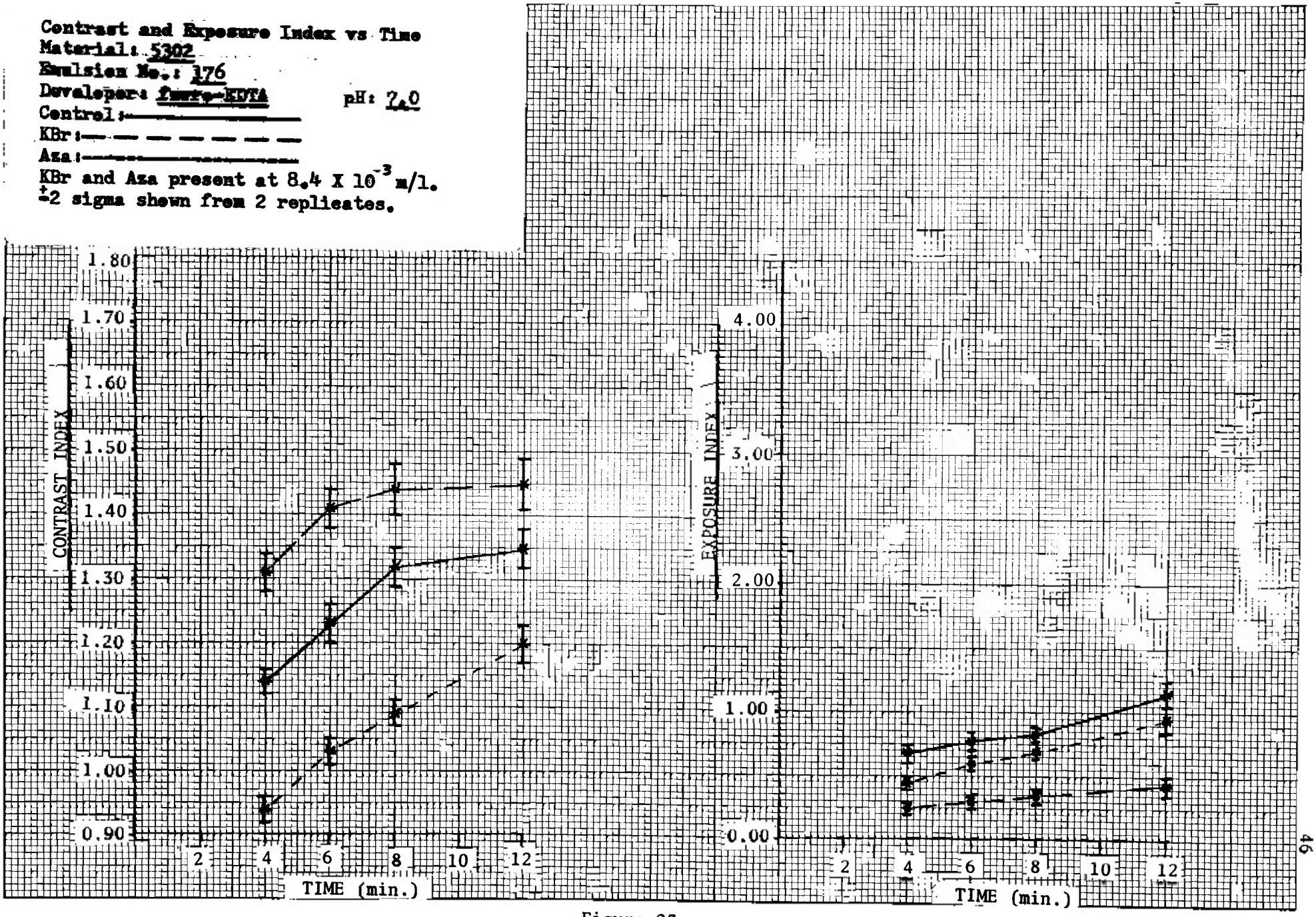

Contrast and Exposure Index vs Time
Material: 5302
Emulsion No.: 176
Developer: Fmuro-EDTA
pH: 7.0
Control:
KBr:
Aza:
KBr and Aza present at 8.4 X 10^-3 m/l.
±2 sigma shown from 2 replicates.
CONTRAST INDEX
1.80
1.70
1.60
1.50
1.40
1.30
1.20
1.10
1.00
0.90
2
4
6
8
10
12
TIME (min.)
EXPOSURE INDEX
4.00
3.00
2.00
1.00
0.00
2
4
6
8
10
12
TIME (min.)

Figure 23

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 4 min. pH: 8.5
Control: ————————
KBr: — — — — —
Aza: ————————
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

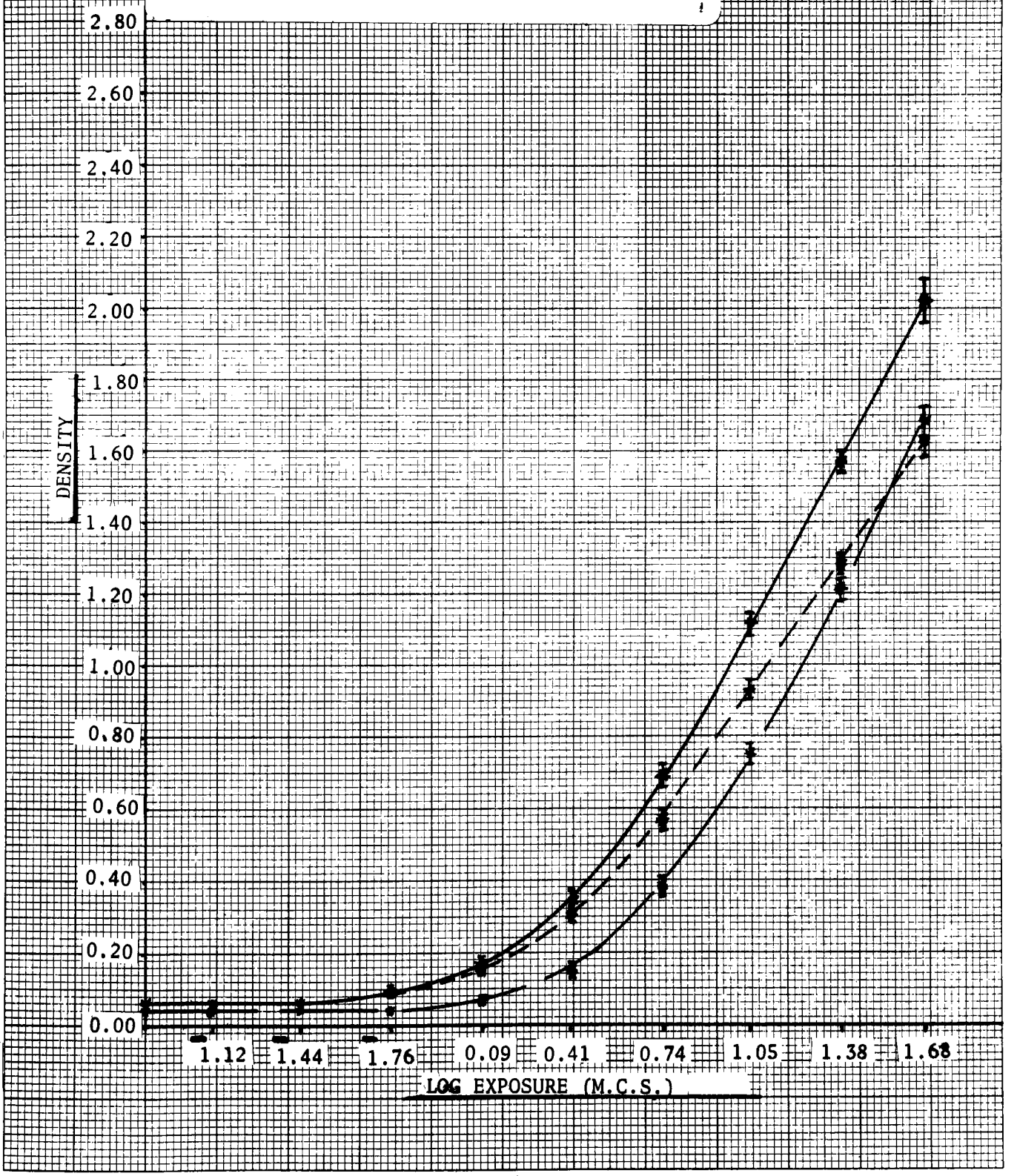


Figure 24

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion no.: 176
Developer: ferro-EDTA Time: 7 min. pH: 8.5
Control: ————————
KBr: — — — — —
Aza: ——————————
KBr and Aza present at 8.4×10^{-3} m/l.
± 2 sigma shown from 2 replicates.

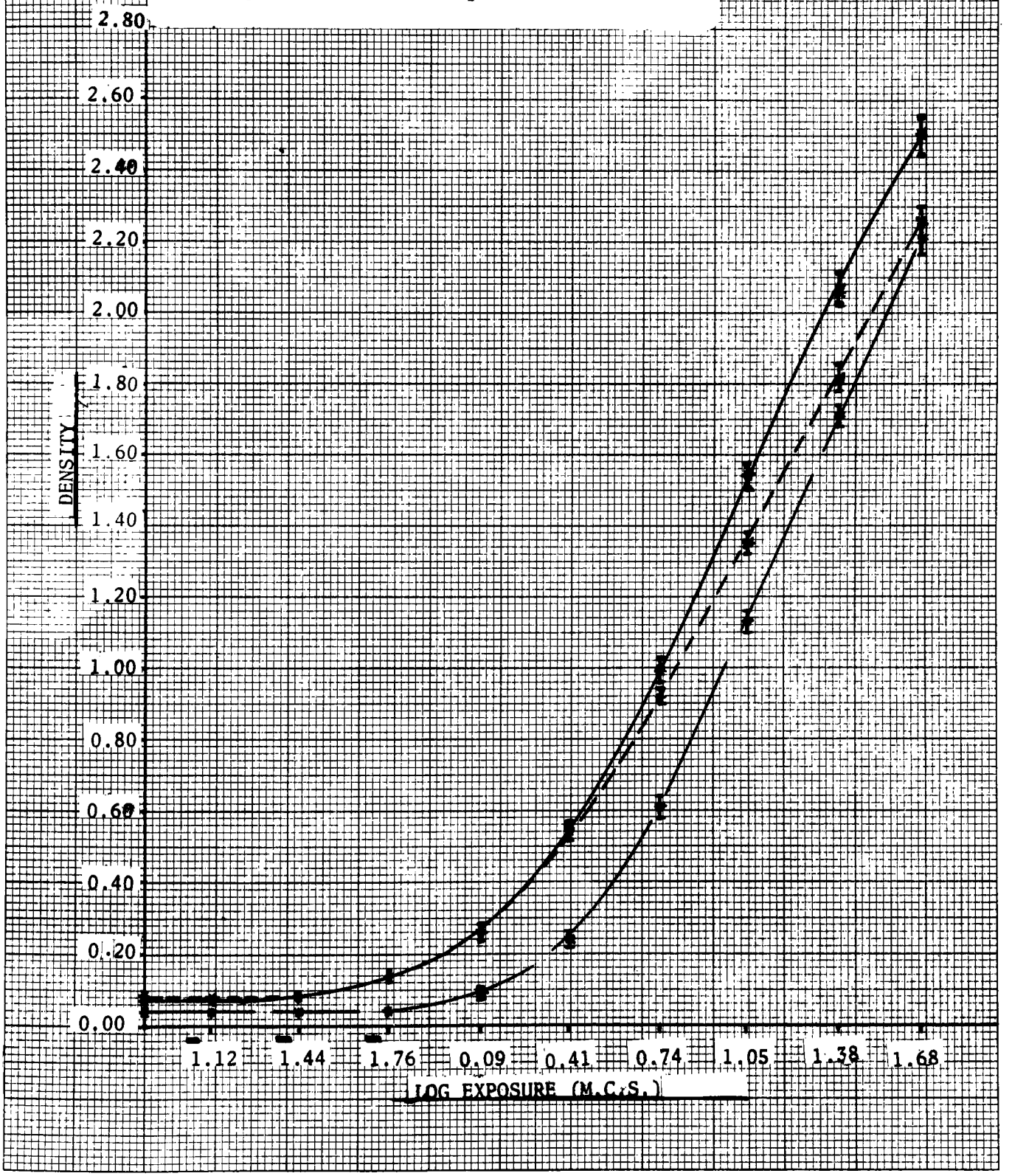


Figure 25

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion no.: 176
Developer: ferro-EDTA Time: 10 min. pH 8.5
Control: ——————
KBr: — — — — —
Aza: ——————
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

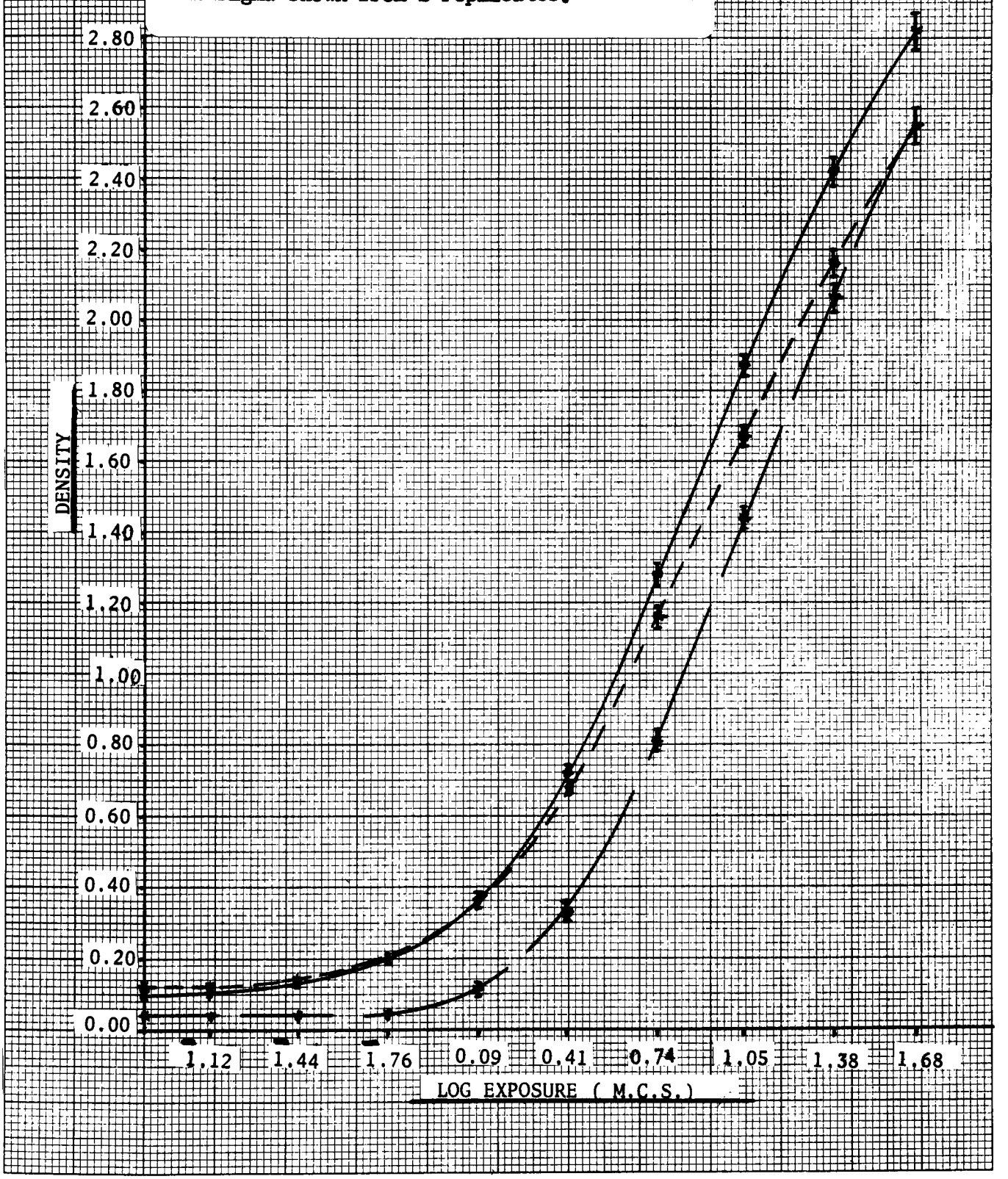


Figure 26

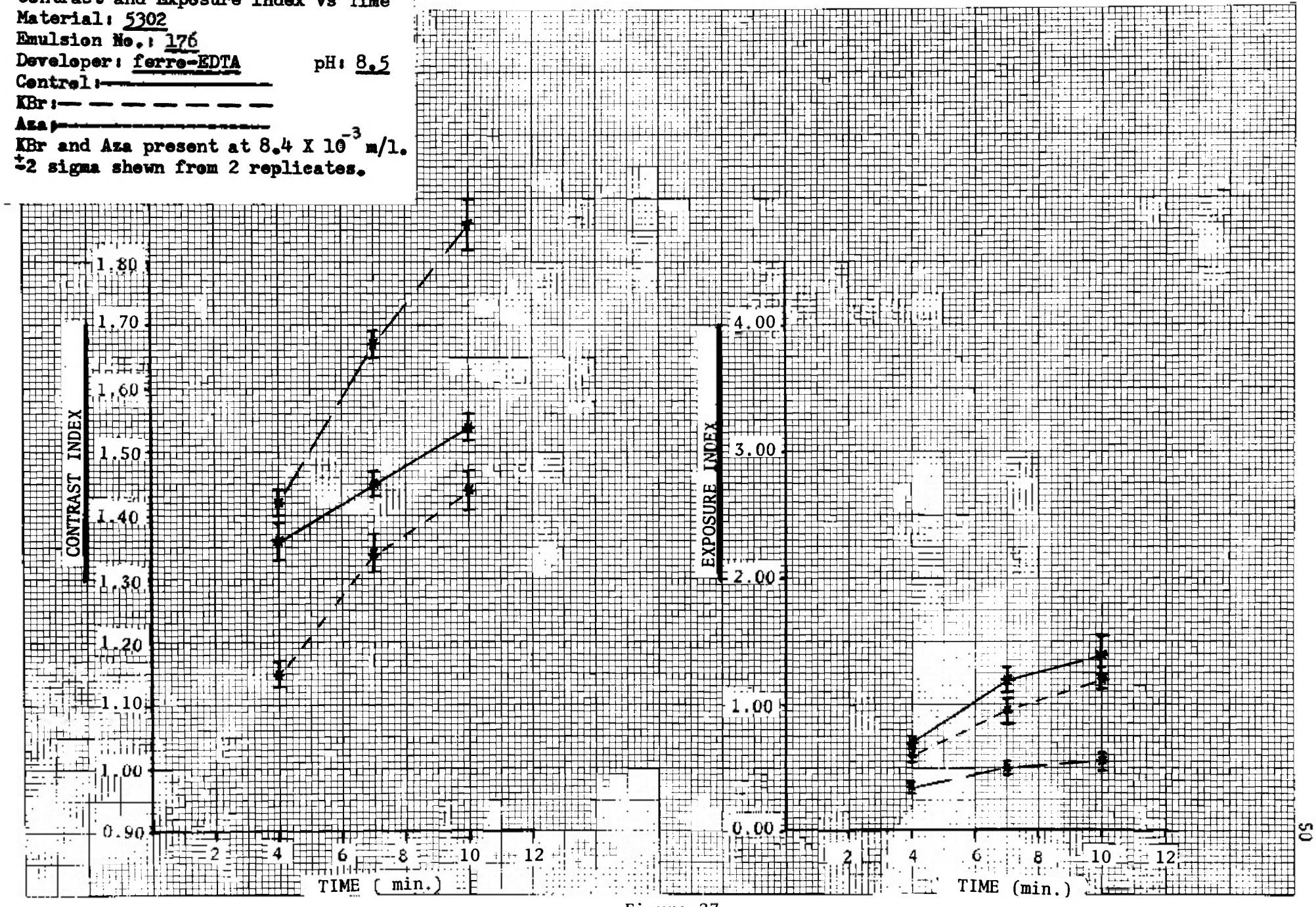

Contrast and Exposure Index vs Time
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA pH: 8.5
Control:
KBr:
Aza:
KBr and Aza present at 8.4 X 10^-3 m/l.
±2 sigma shown from 2 replicates.
CONTRAST INDEX
1.80
1.70
1.60
1.50
1.40
1.30
1.20
1.10
1.00
0.90
2
4
6
8
10
12
TIME (min.)
EXPOSURE INDEX
4.00
3.00
2.00
1.00
0.00
2
4
6
8
10
12
TIME (min.)

Figure 27

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 4 min. pH: 10.0
Control: ———————
KBr: — — — — —
Aza: - - - - - - - - - - -
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

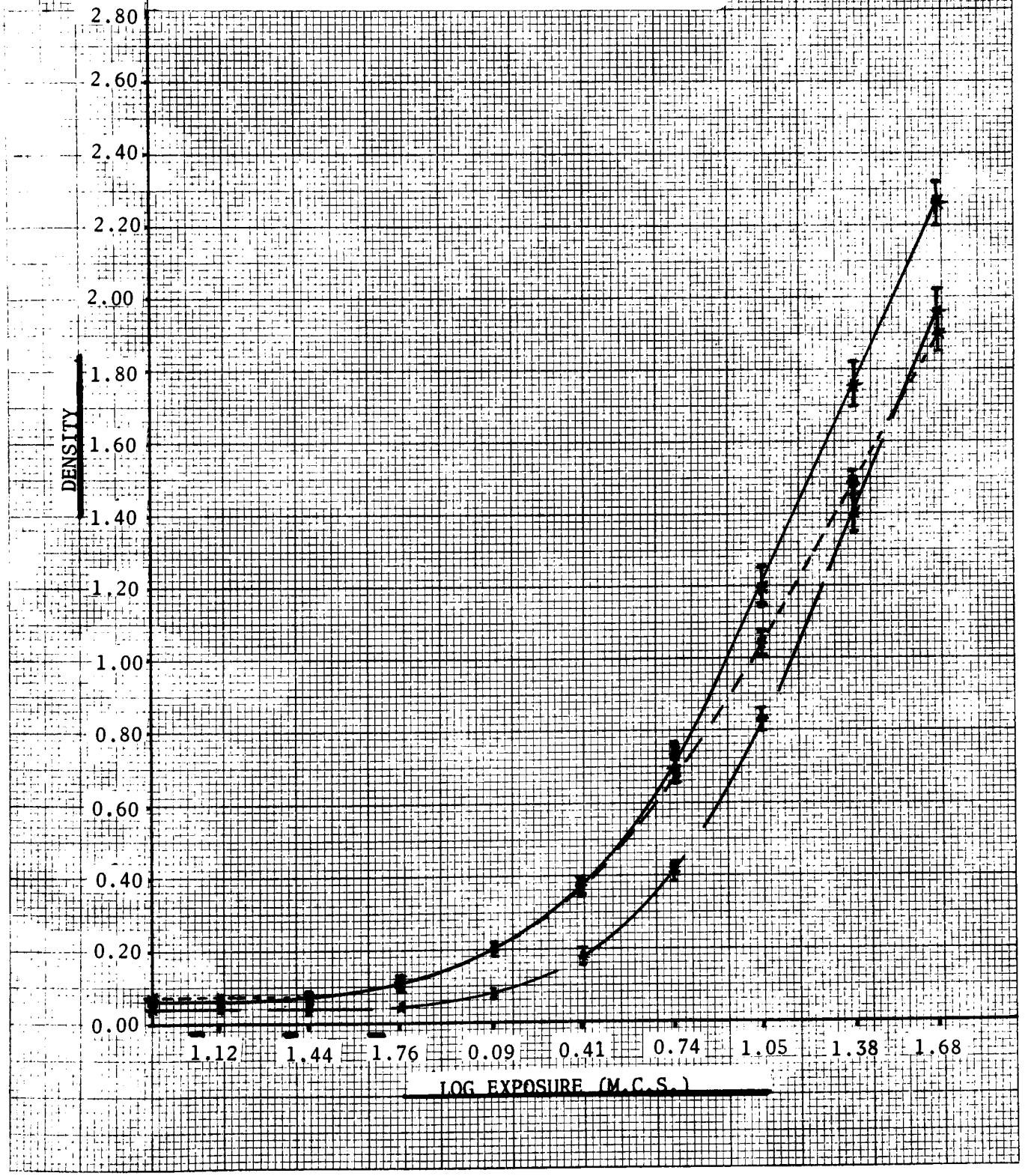


Figure 28

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 6 min. pH: 10.0
Control:————————
KBr:— — — — —
Aza:— — — — — —
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

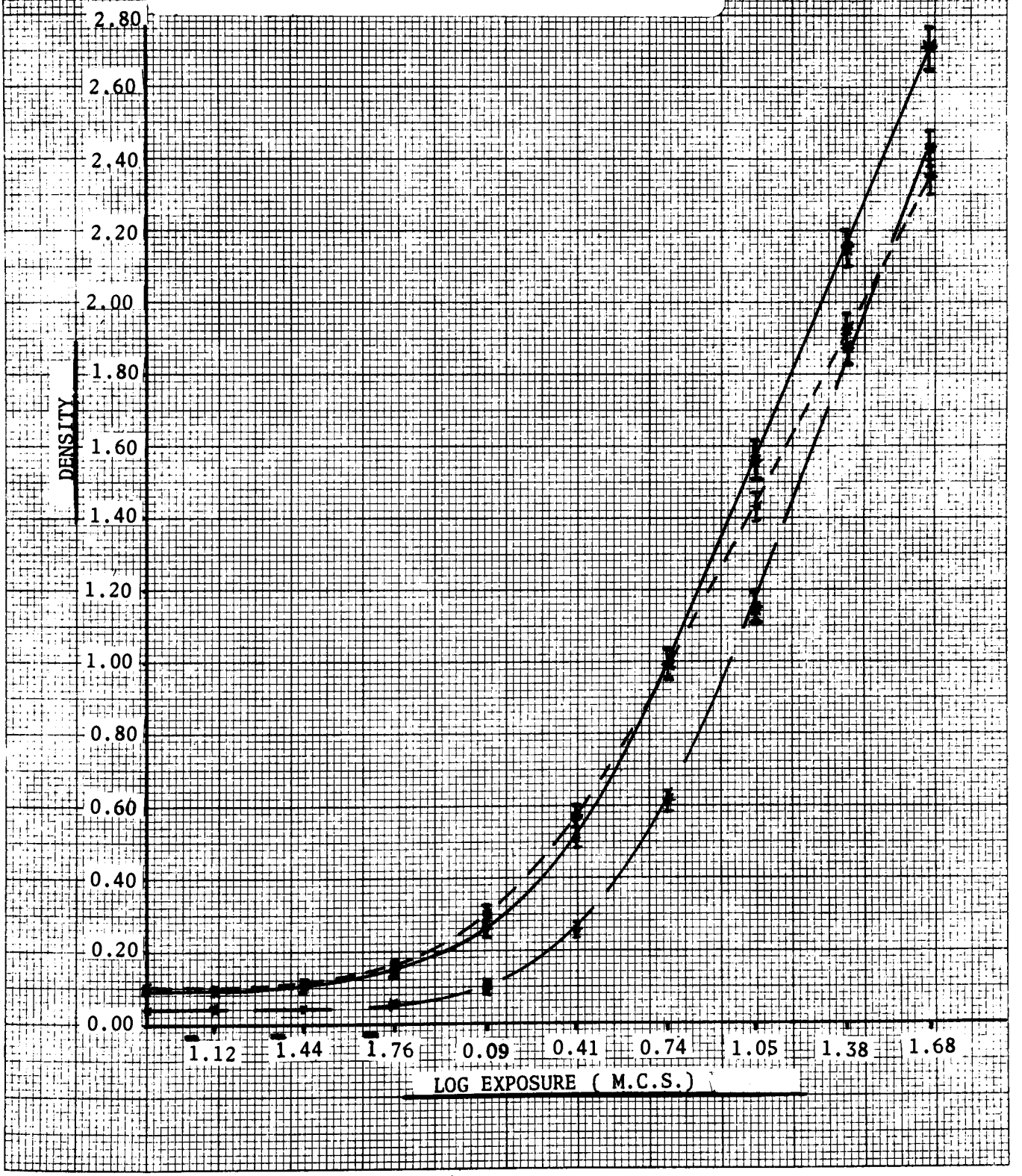


Figure 29

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 8 min. pH: 10.0
Control: ————————
KBr: — — — — —
Aza: ——————————
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

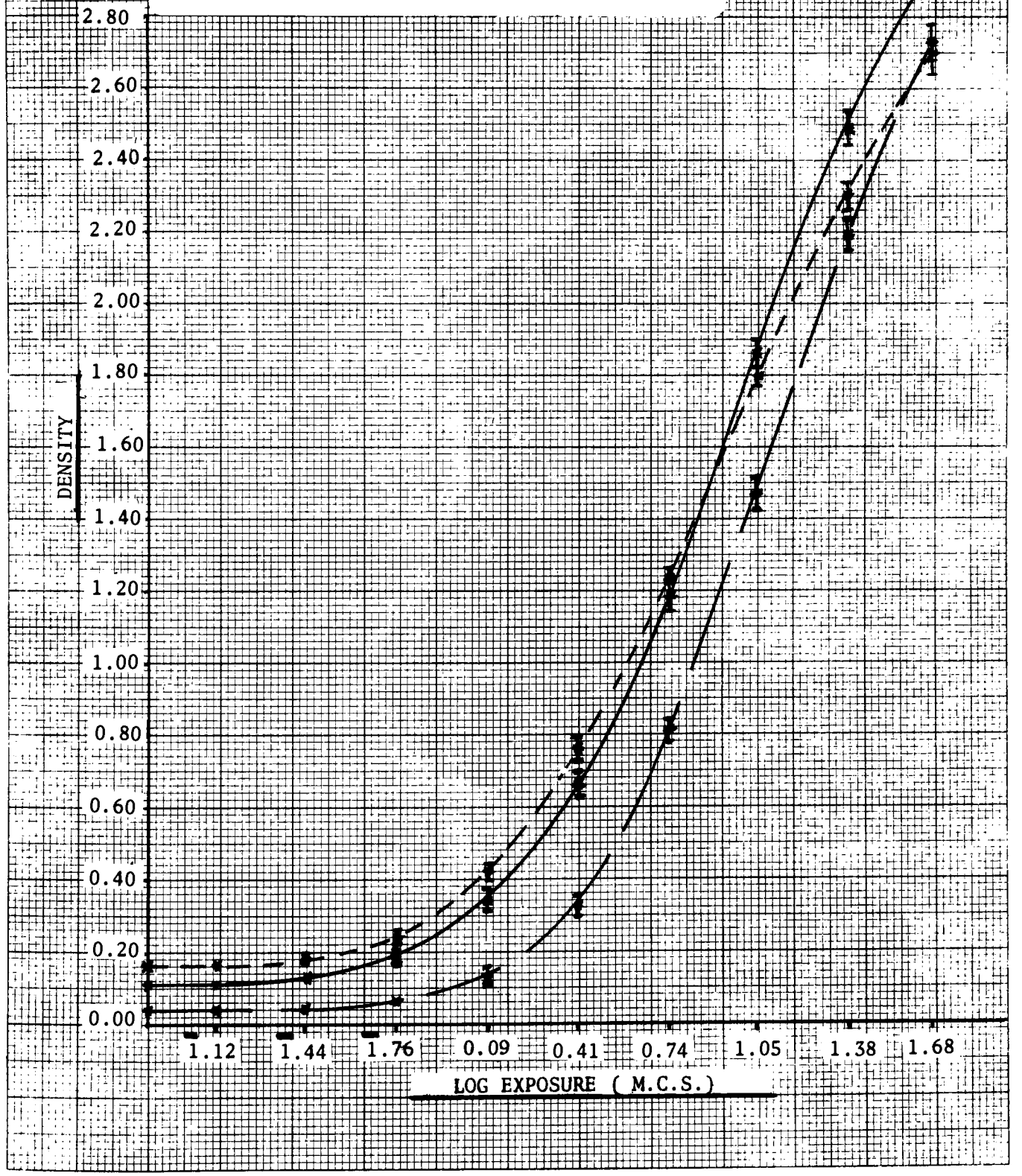


Figure 30

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 12 min. pH: 10.0
Control: ————————
KBr: — — — — —
Aza: ——————————
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

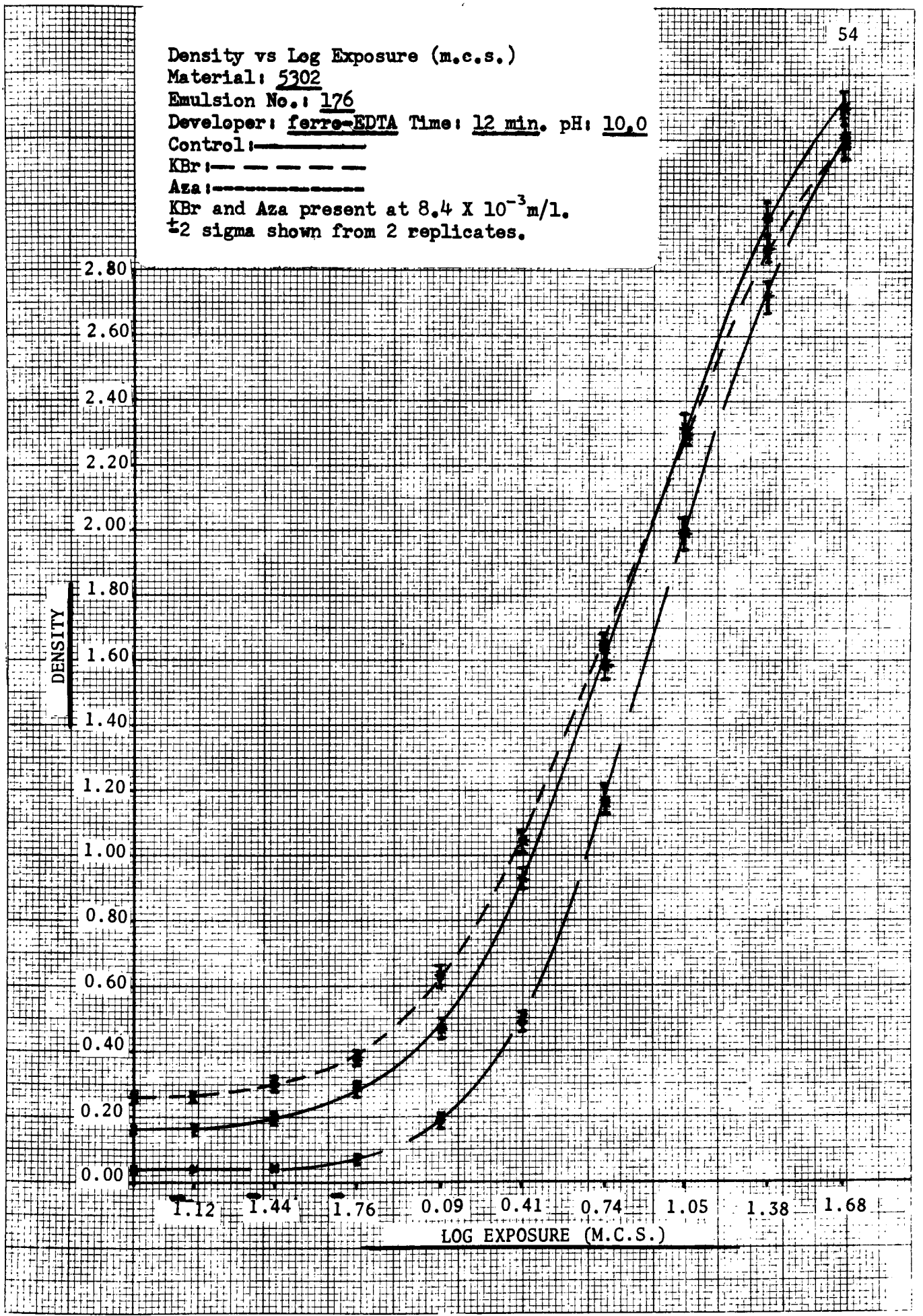


Figure 31

Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA pH: 10.0
Control: ————————
KBr: — — — — — — —
Aza: ————————
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

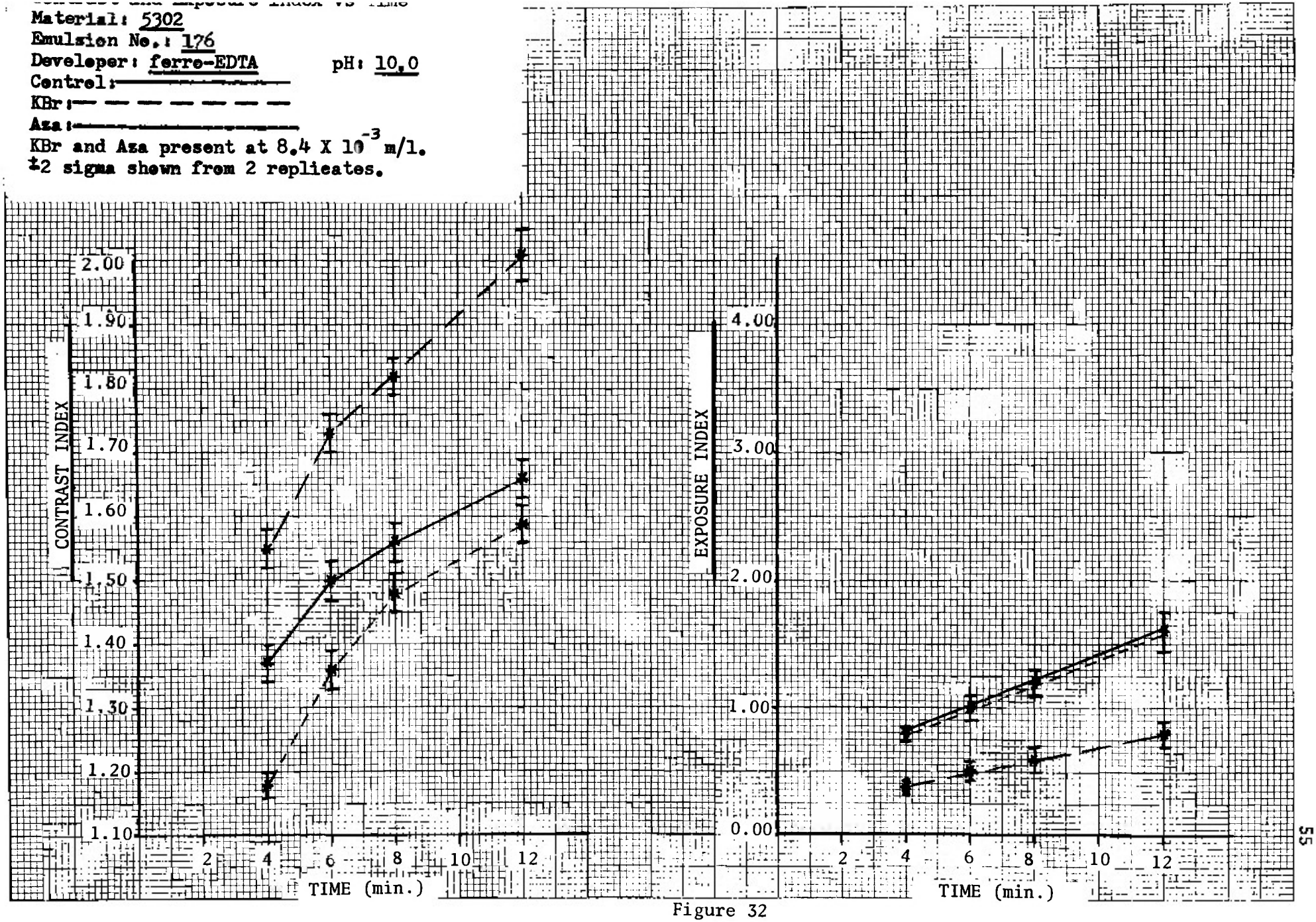


Figure 32

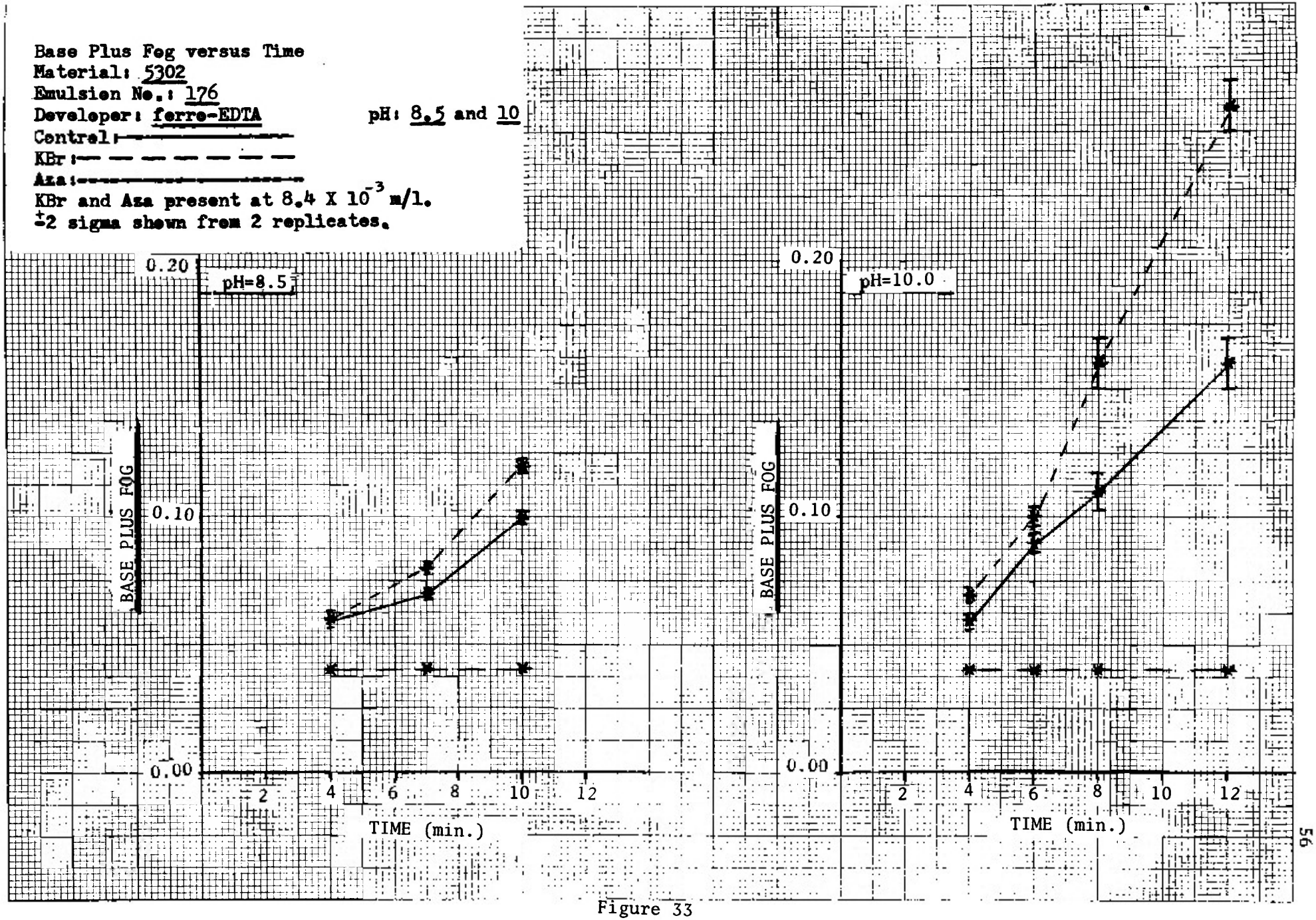

Base Plus Fog versus Time
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA
pH: 8.5 and 10
Control:
KBr:
Aza:
KBr and Aza present at 8.4 X 10^-3 m/l.
±2 sigma shown from 2 replicates.
pH=8.5
pH=10.0
BASE PLUS FOG
0.20
0.10
0.00
2
4
6
8
10
12
TIME (min.)

Figure 33

At pH 10.0 a marked change in the effect of Aza on development occurred from that noted at the lower pH values. The high densities were still slightly reduced by Aza, but the low densities were not suppressed at all. The acceleration of fog formation in the presence of Aza was even greater than at pH 8.5. KBr behaved as it did before indicating its activity is relatively independent of pH.

Figure 33 shows the base plus fog versus time curves at pH 8.5 and at pH 10.0.

The preceding evidence indicates that the ability of Aza to function as an antifoggant under those conditions decreased with increasing pH. In fact, at high pH values it even accelerated fog formation.

pH Study of 5060 Film Processed in Fe-EDTA

Experimental Procedure was exactly the same as before with the exception of the lower pH limit and the development times. The lowest pH tested was 4.66 instead of 4.46. This was not intentional, but the two values were close enough for comparable results. Development times were arbitrarily chosen at 2, 4, and 6 minutes. Since 5060 developed slower than 5302, these shorter times of development yielded results comparable to a lower fraction of gamma infinity than 5302. The 5060 had an emulsion number 071-5. Results: Figures 34 through 37 are the results at pH 4.66. The 5060 film had a gray antihalation base with a density of 0.25.

Density vs Log Exposure (m.c.s.)
Material: 5060
Emulsion No.: 071-5
Developer: ferro-EDTA Time: 2 min. pH: 4.66
Control: ————————
KBr: — — — — —
Aza: ——————————
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

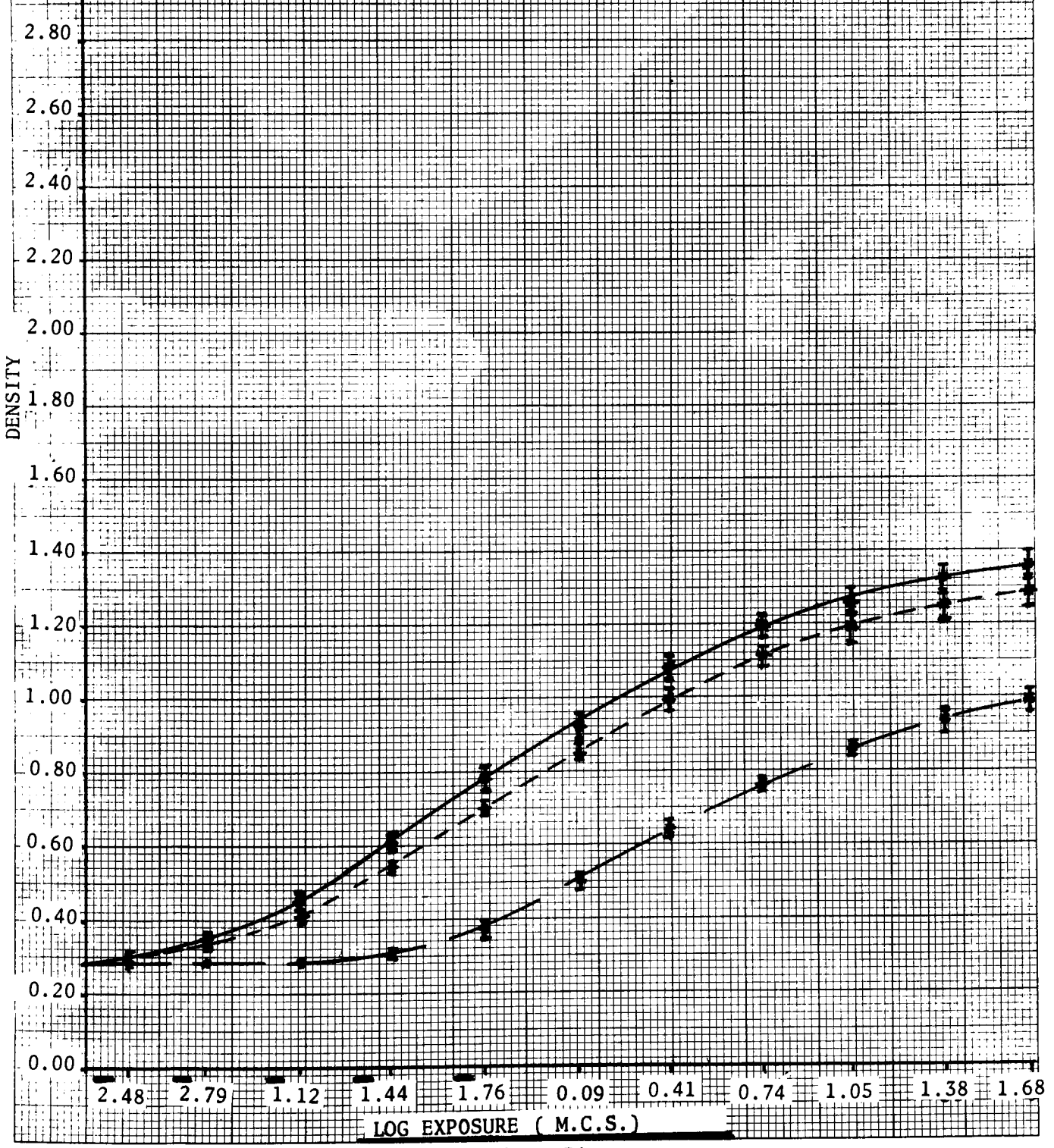


Figure34

Density vs Log Exposure (m.c.s.)
Material: 5060
Emulsion no.: 071-5
Developer: ferro-EDTA Time: 4 min. pH: 4.66
Control: ————————
KBr: — — — — —
Aza: ————————
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

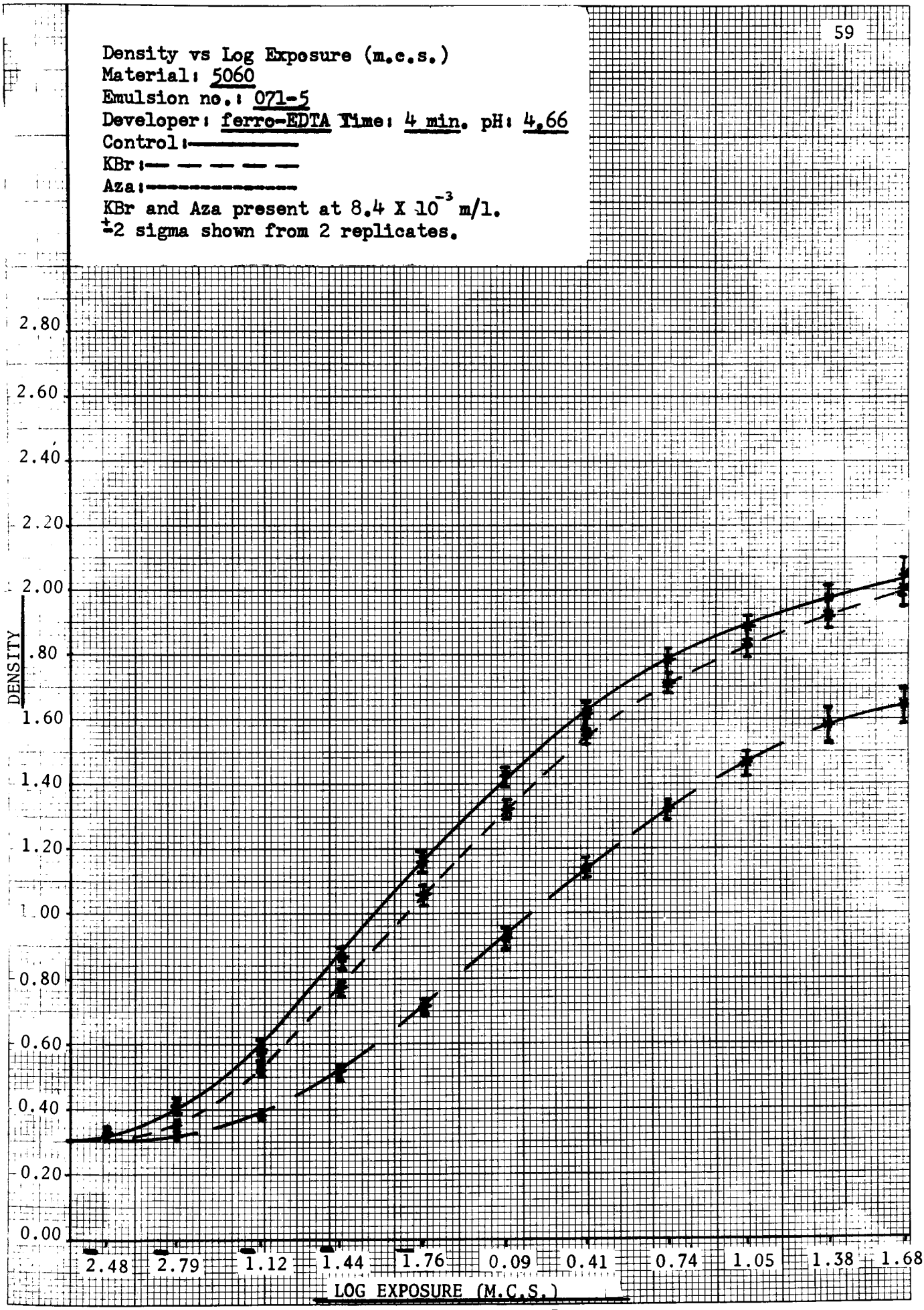


Figure 35

Density vs Log Exposure (m.c.s.)
Material: 5060
Emulsion No.: 071-5
Developer: ferro-EDTA Time: 6 min. pH: 4.66
Control:————————
KBr:— — — — —
Aza:-----------
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

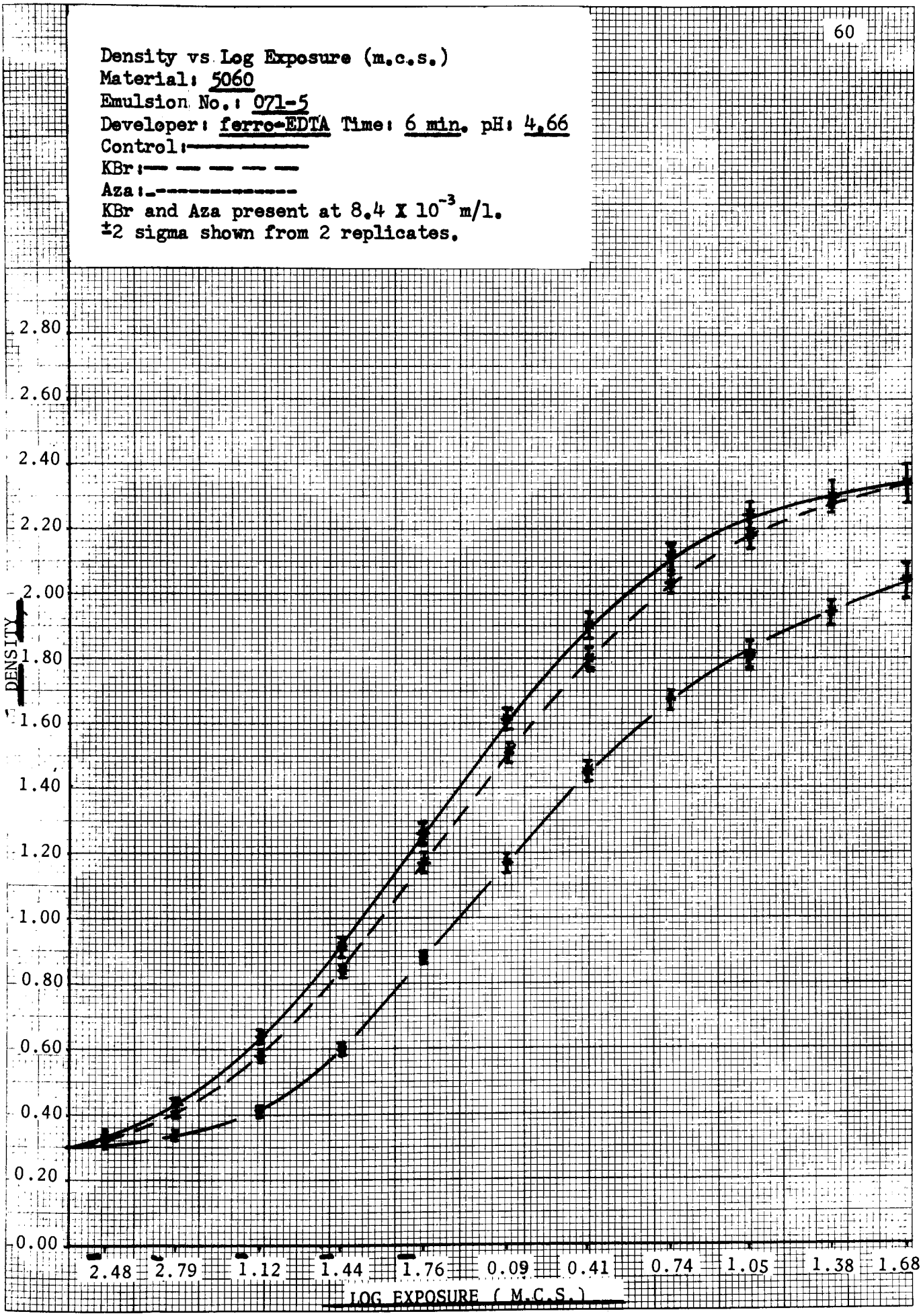


Figure 36

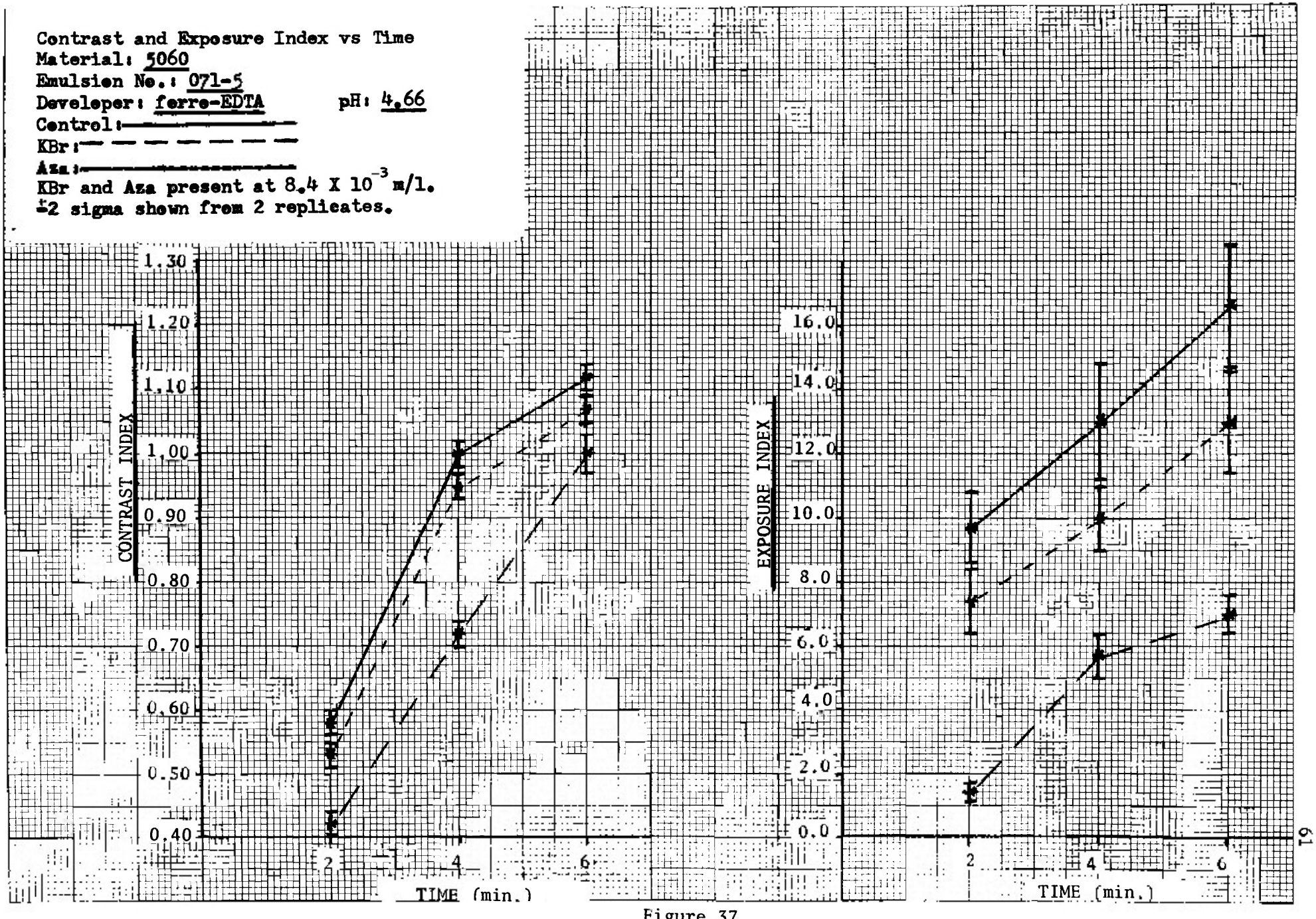

Contrast and Exposure Index vs Time
Material: 5060
Emulsion No.: 071-5
Developer: ferro-EDTA pH: 4.66
Control:
KBr:
Aza:
KBr and Aza present at 8.4 X 10^-3 m/l.
±2 sigma shown from 2 replicates.
CONTRAST INDEX
1.30
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
0.40
2
4
6
TIME (min.)
EXPOSURE INDEX
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
2
4
6
TIME (min.)

Figure 37

At pH 4.66 both Aza and KBr restrained development of the 5060 Film as before on the 5302 Film. KBr was more effective in decreasing speed as before, however, on the 5060 film it reduced contrast index more than Aza.

Figures 38 through 41 are the results at pH 7.0.

At pH 7.0 Aza and KBr restrained development as before. There was still no appreciable fog to suppress. The restraining ability of KBr on contrast index decreased with time whereas the restraint by Aza remained fairly constant.

Figures 42 through 45 are the results at pH 8.5.

At pH 8.5 a slight increase in developer activity was noted by the increase in contrast index and fog level. Aza and KBr reduced speed and fog. Aza reduced the higher densities more than KBr for the 6 minute development time as it did consistently with the 5302 Film. The greater reduction of the higher densities by Aza is more noticeable with more complete development.

Figures 46 through 49 are the results at pH 10.0.

At pH 10.0 the fog level increased. Aza and KBr reduced both fog and speed. KBr was more effective in its antifoggant action than Aza, but Aza still showed its tendency to suppress higher densities more than KBr.

Density vs Log Exposure (m.c.s.)
Material: 5060
Emulsion No.: 071-5
Developer: ferro-EDTA Time: 2 min. pH: 7.0
Control: ————————
KBr: — — — — —
A_Za: ————————
KBr and A_Za present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

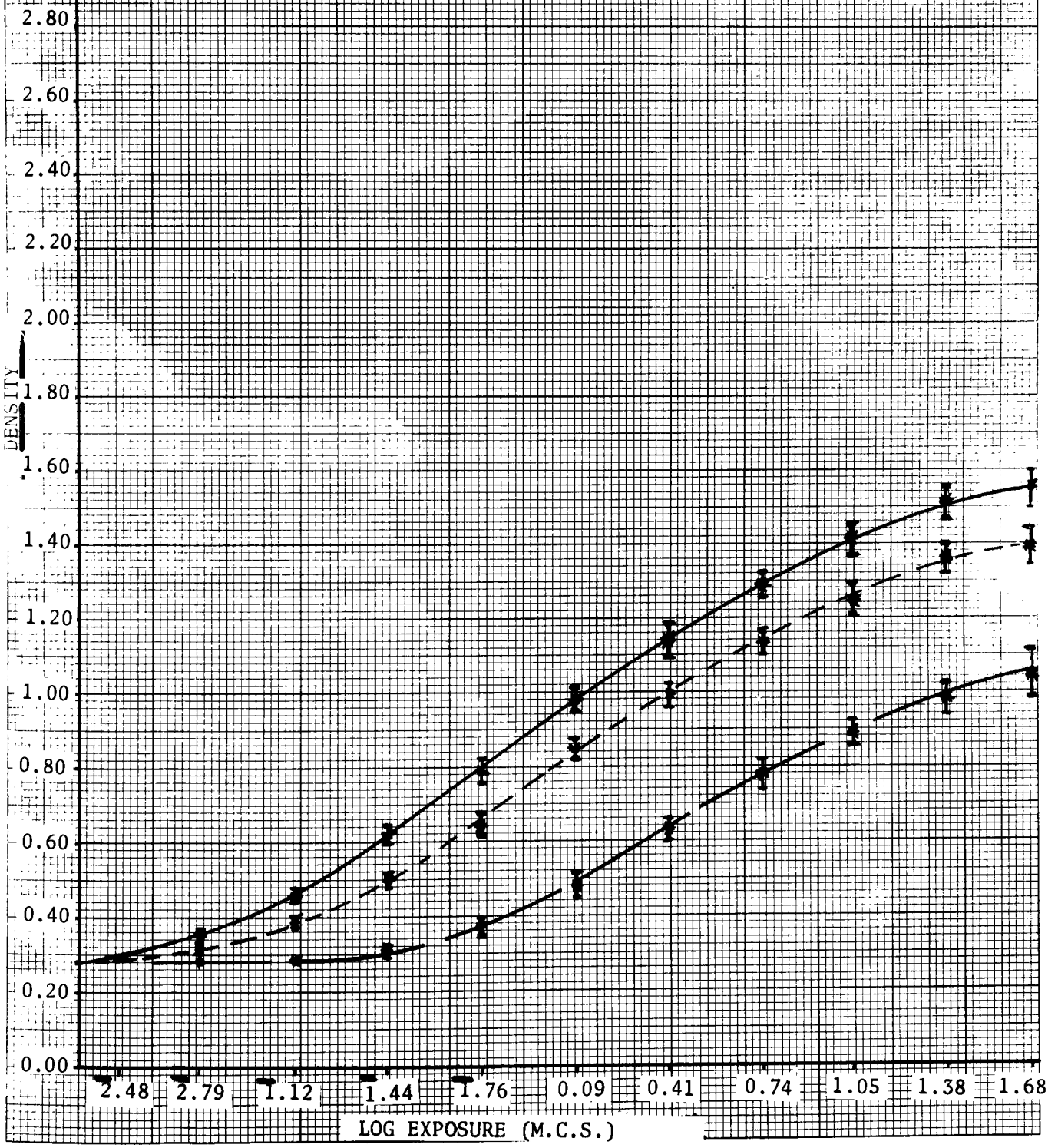


Figure 38

Density vs Log Exposure (m.c.s.)
Material: 5060
Emulsion No.: 071-5
Developer: ferro-EDTA Time: 4 min. pH: 7.0
Control:————————
KBr:— — — — —
Aza:----------
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

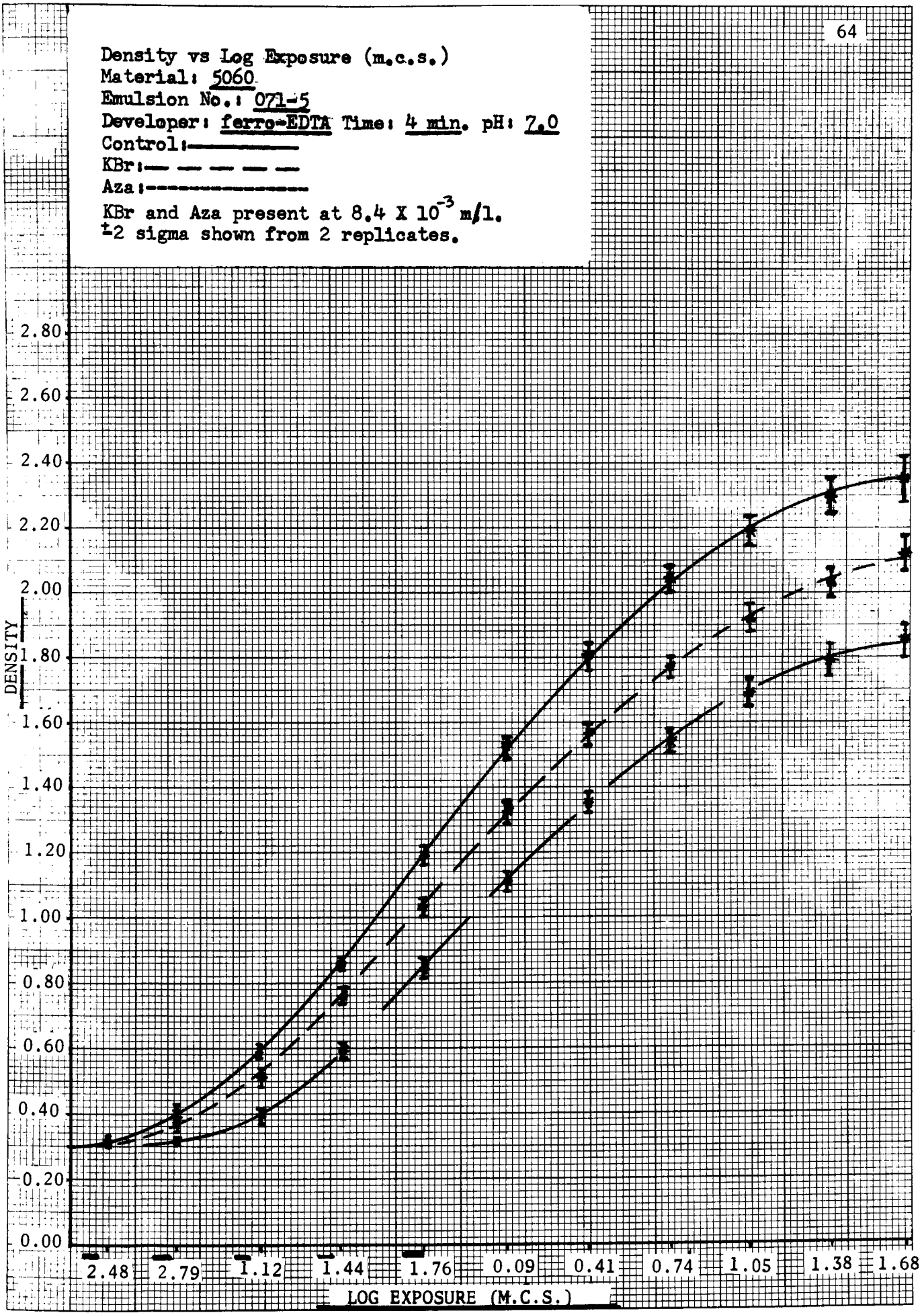


Figure 39

Density vs Log Exposure (m.c.s.)
Material: 5060
Emulsion No.: 071-5
Developer: ferro-EDTA Time: 6 min. pH: 7.0
Control:————————
KBr:— — — — —
Aza:— — — — — —
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

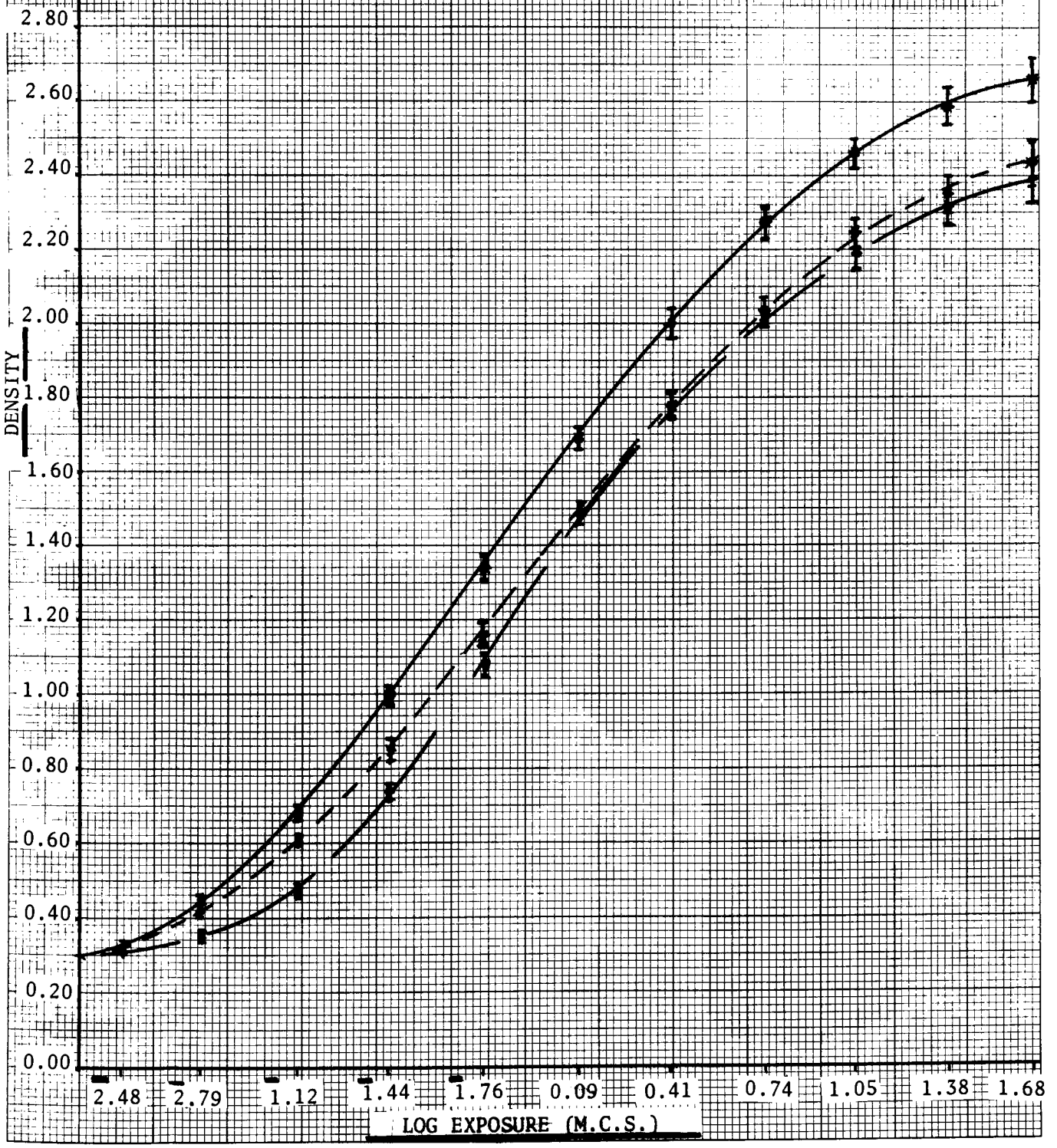


Figure 40

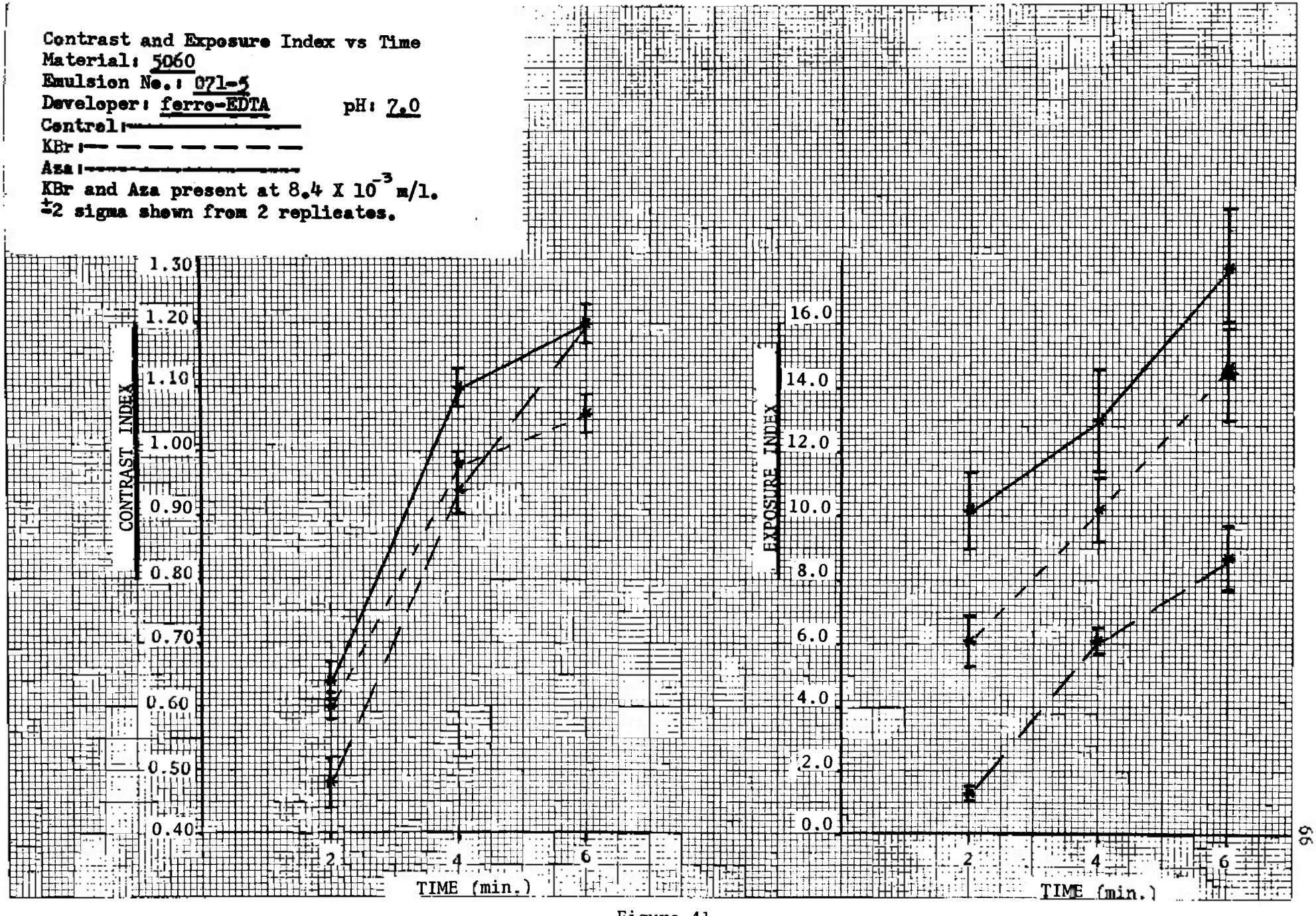

Contrast and Exposure Index vs Time
Material: 5060
Emulsion No.: 071-5
Developer: ferro-EDTA pH: 7.0
Control:
KBr:
Aza:
KBr and Aza present at 8.4 X 10^-3 m/l.
±2 sigma shown from 2 replicates.
CONTRAST INDEX
1.30
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
0.40
2
4
6
TIME (min.)
EXPOSURE INDEX
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
2
4
6
TIME (min.)

Figure 41

Density vs Log Exposure (m.c.s.)
Material: 5060
Emulsion No.: 071-5
Developer: ferro-EDTA Time: 2 min. pH: 8.5
Control: ————————
KBr: — — — — —
Aza: - - - - - - - - - - - -
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

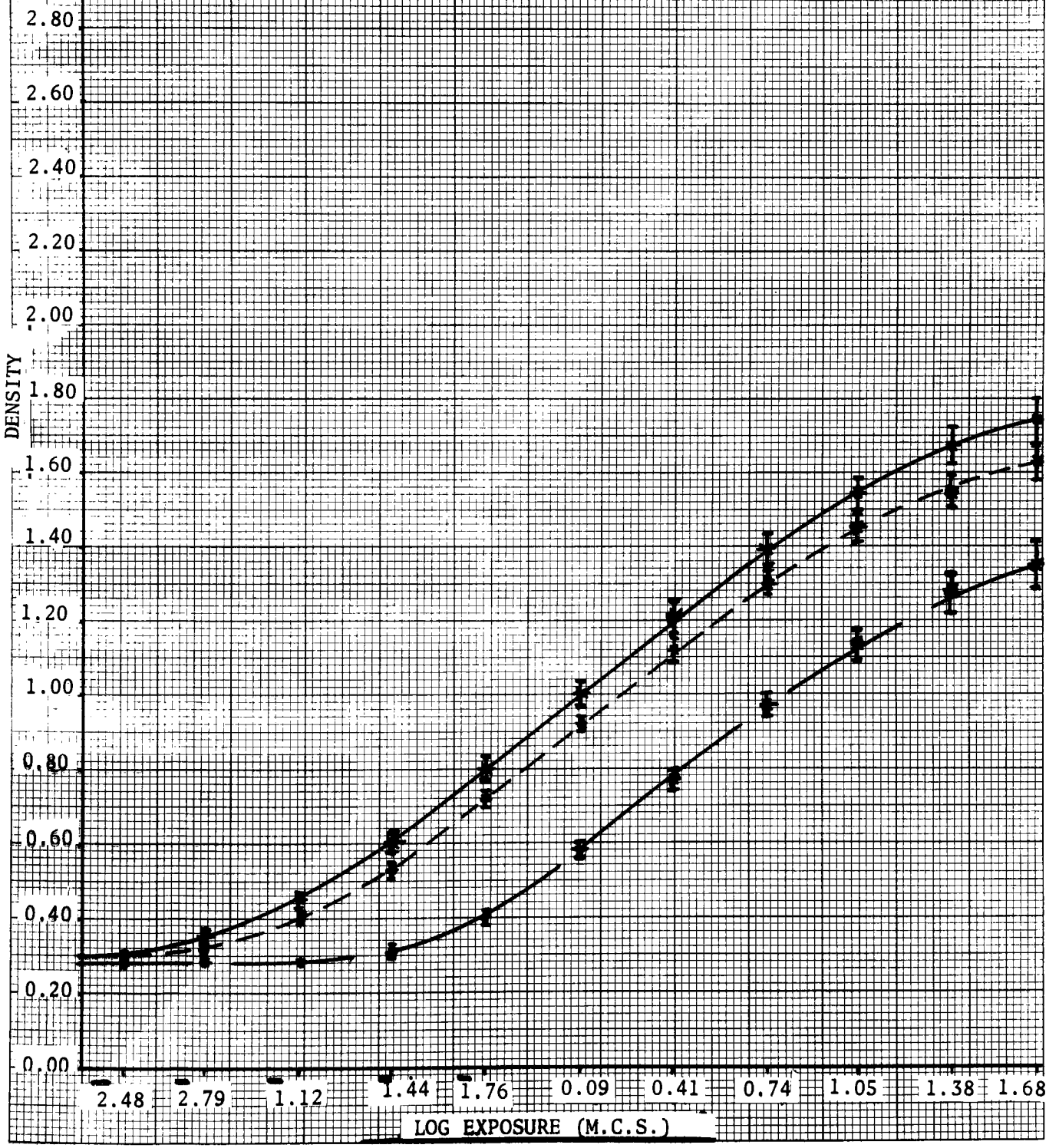


Figure 42

Density vs Log Exposure (m.c.s.)
Material: 5060
Emulsion No.: 071-5
Developer: ferro-EDTA Time: 4 min. pH: 8.5
Control: ————————
KBr: — — — — —
Aza: - - - - - - - - - - -
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

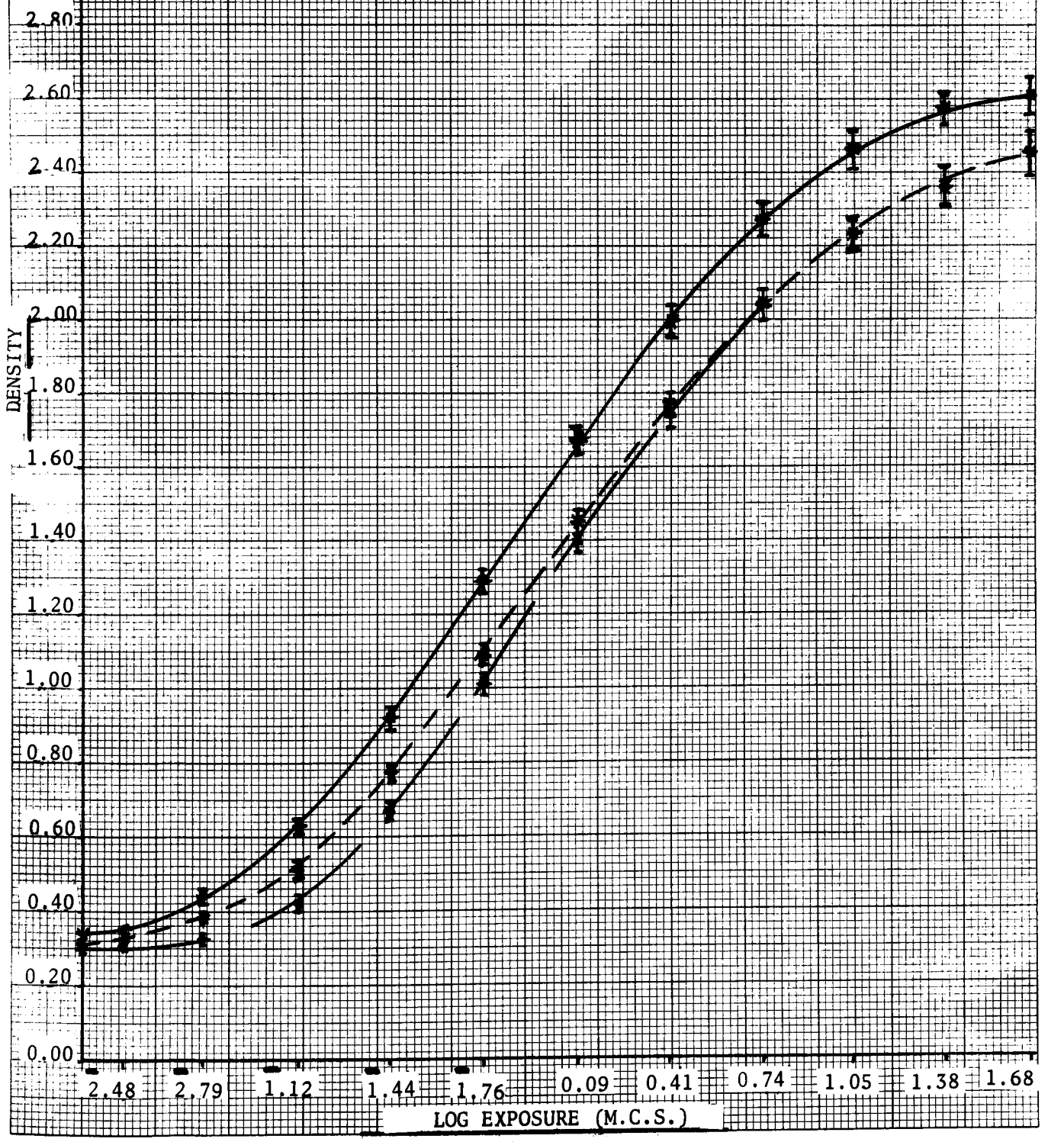


Figure 43

Density vs Log Exposure (m.c.s.)
Material: 5060
Emulsion No.: 071-5
Developer: ferro-EDTA Time: 6 min. pH: 8.5
Control:————————
KBr:— — — — —
Aza:————————
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

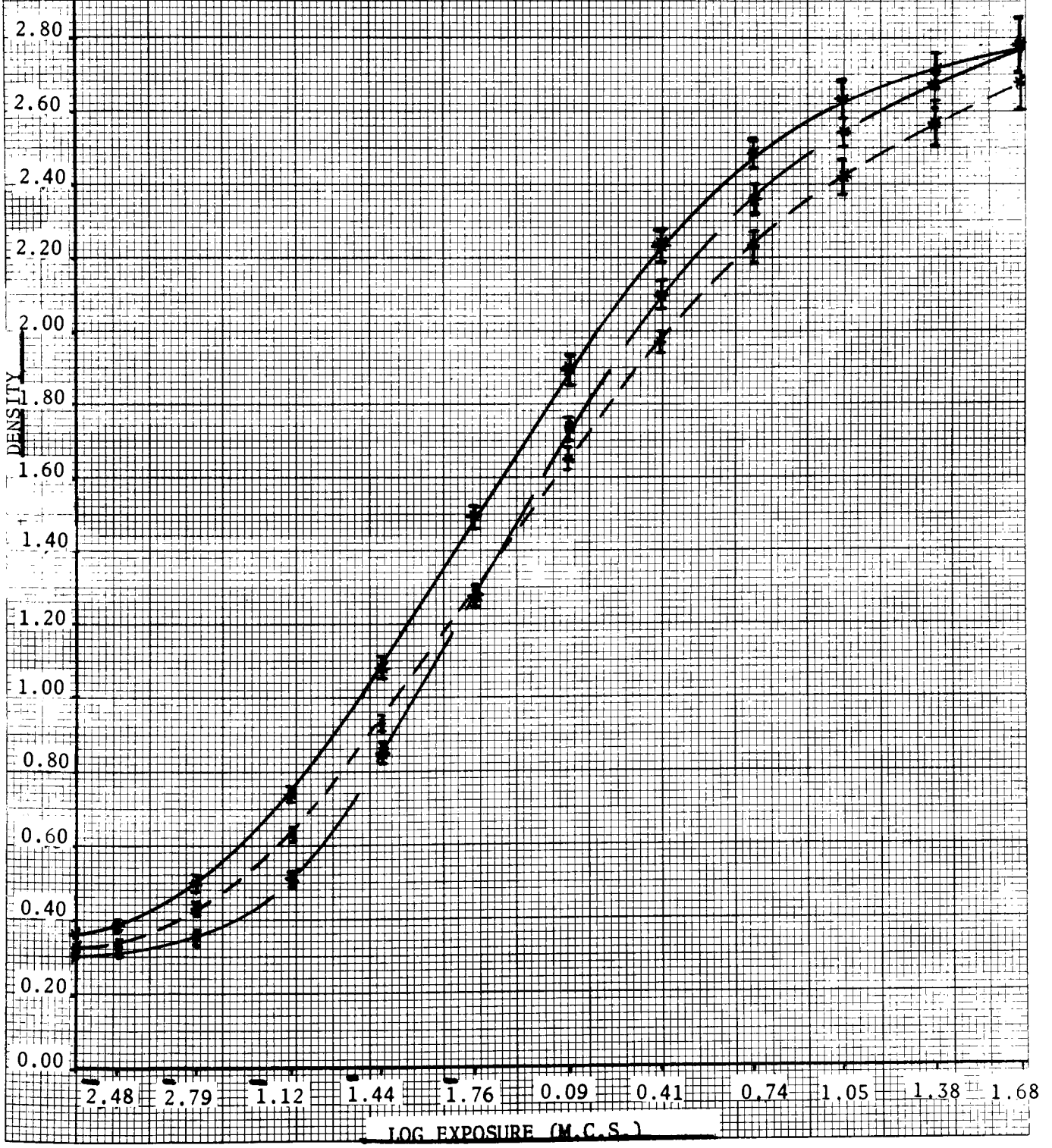


Figure 44

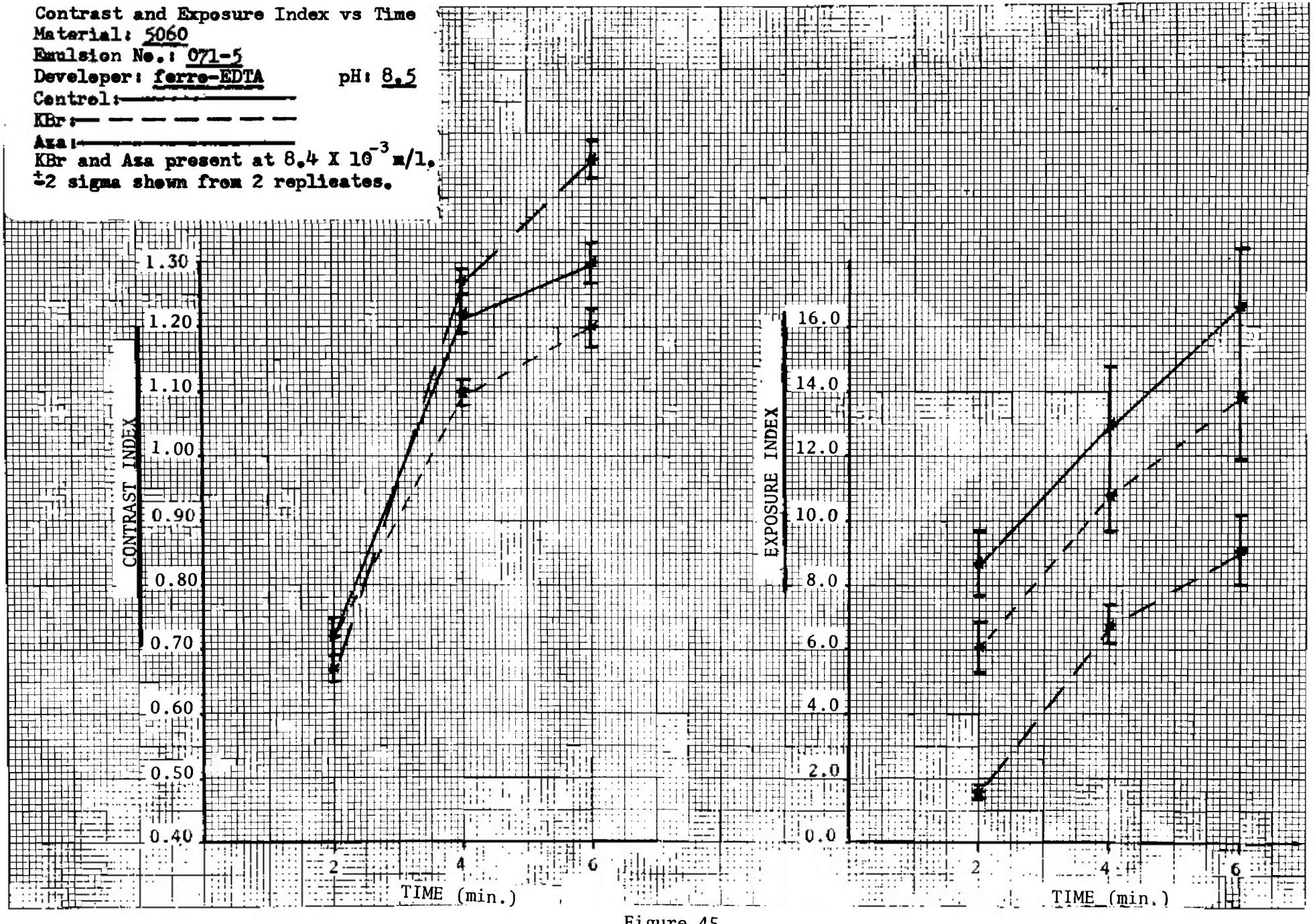

Contrast and Exposure Index vs Time
Material: 5060
Emulsion No.: 071-5
Developer: ferro-EDTA pH: 8.5
Control:
KBr:
Aza:
KBr and Aza present at 8.4 X 10^-3 m/l.
±2 sigma shown from 2 replicates.
CONTRAST INDEX
1.30
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
0.40
TIME (min.)
2
4
6
EXPOSURE INDEX
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
TIME (min.)
2
4
6

Figure 45

Density vs Log Exposure (m.c.s.)
Material: 5060
Emulsion No.: 071-5
Developer: ferro-EDTA Time: 2 min. pH: 10.0
Control: ————————
KBr: — — — — —
Aza: ————————
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

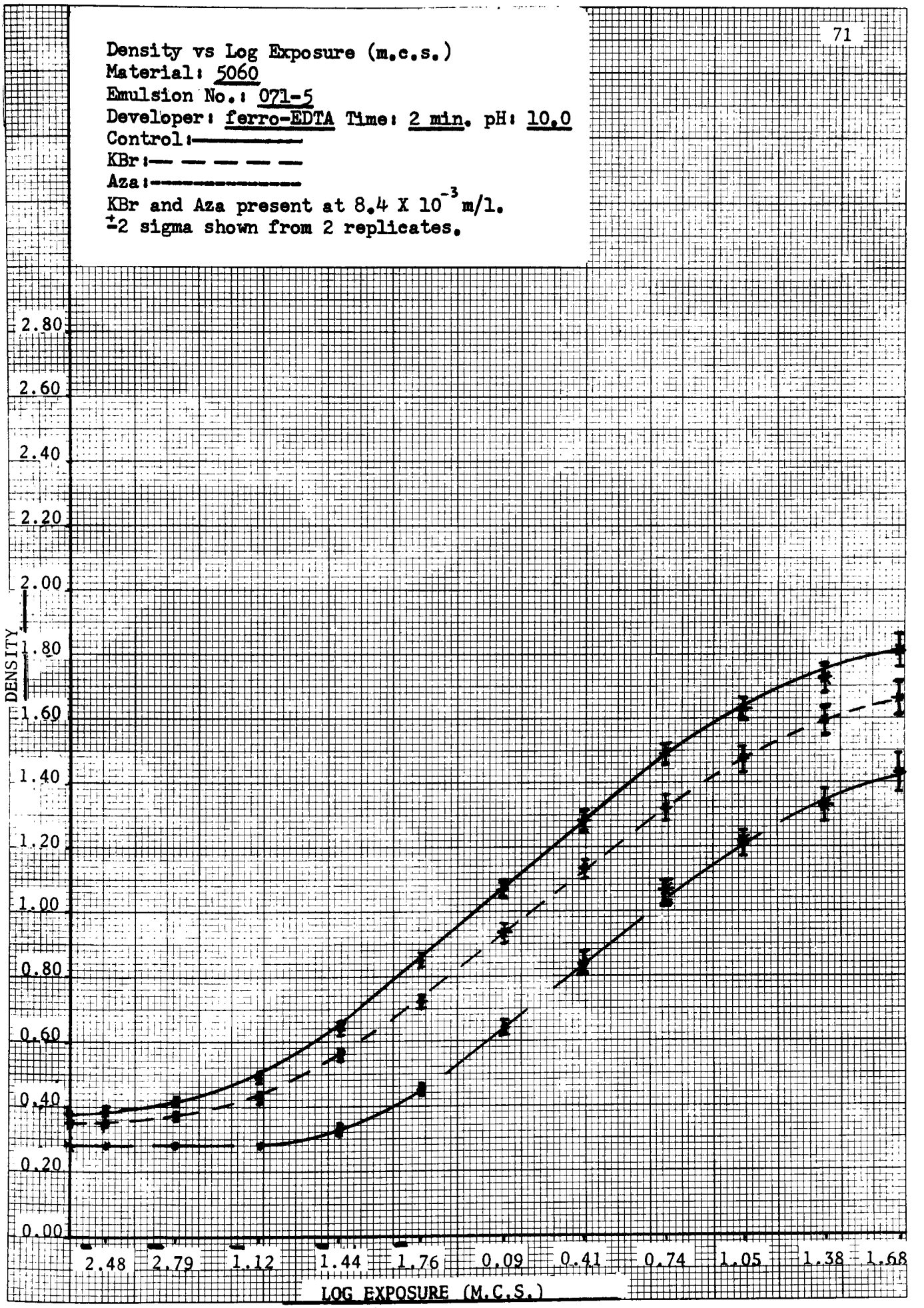


Figure 46

Density vs Log Exposure (m.c.s.)
Material: 5060
Emulsion No.: 071-5
Developer: ferro-EDTA Time: 4 min. pH: 10.0
Control: ————————
KBr: — — — — —
Aza: ——————————

KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

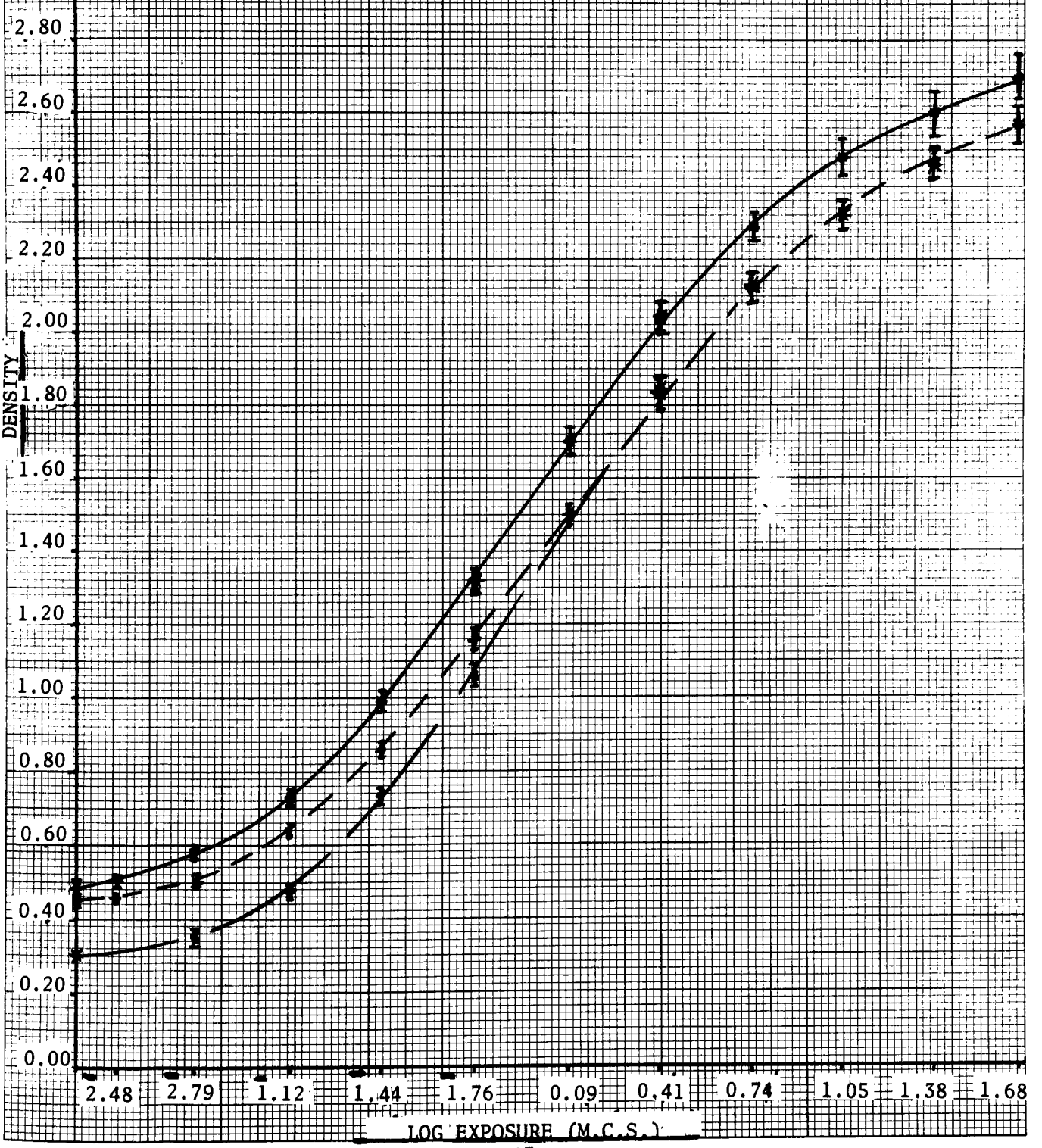


Figure 47

Density vs Log Exposure (m.c.s.)
Material: 5060
Emulsion No.: 071-5
Developer: ferro-EDTA Time: 6 min. pH: 10.0
Control: ————————
KBr: — — — — —
Aza: ——————————
KBr and Aza present at 8.4 X 10^{-3} m/l.
±2 sigma shown from 2 replicates.

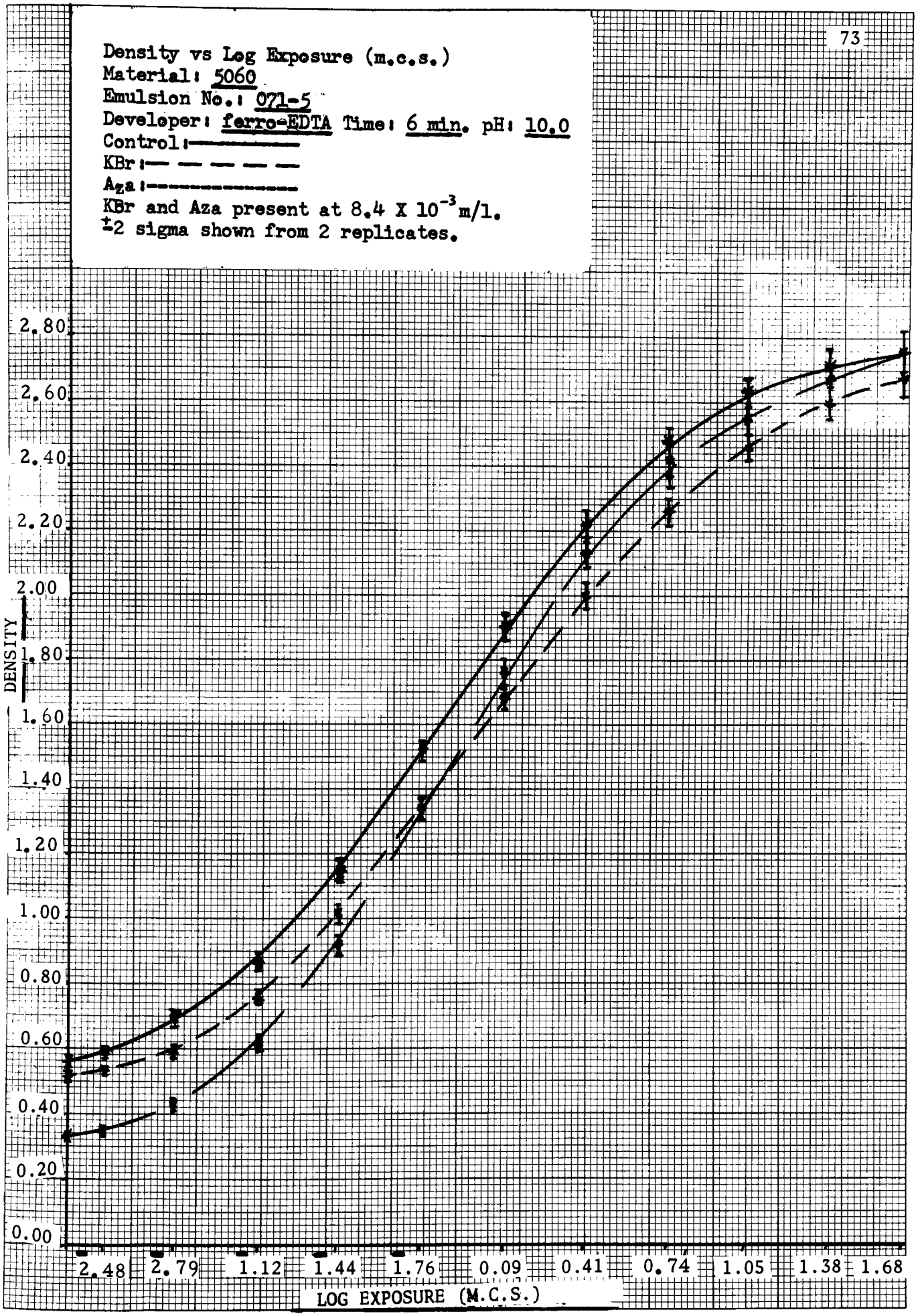


Figure 48

Contrast and Exposure Index vs Time
Material: 5060
Emulsion No.: 071-5
Developer: ferro-EDTA pH: 10.0
Control: ——————
KBr: — — — — — — —
Aza: ——————————
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

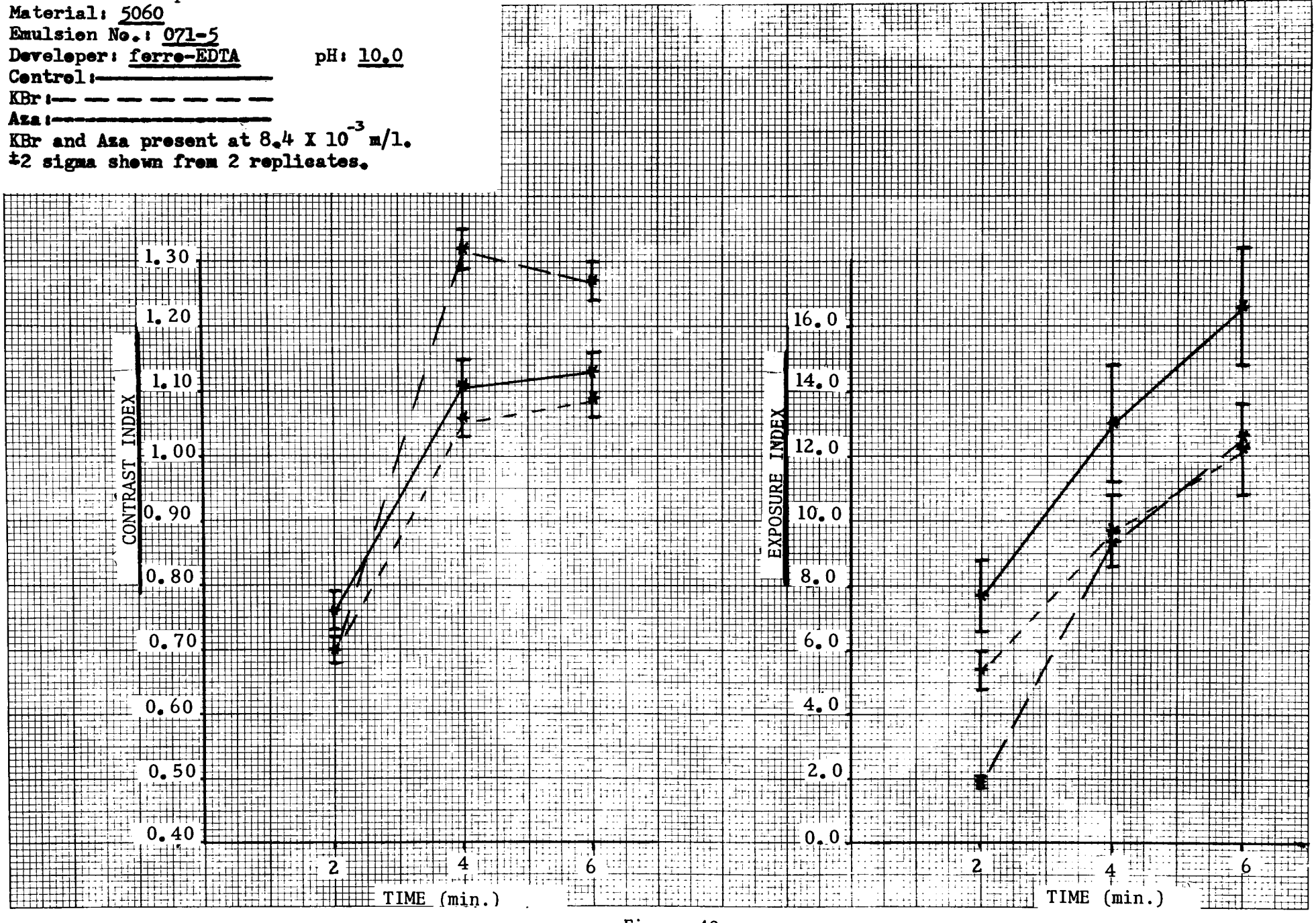


Figure 49

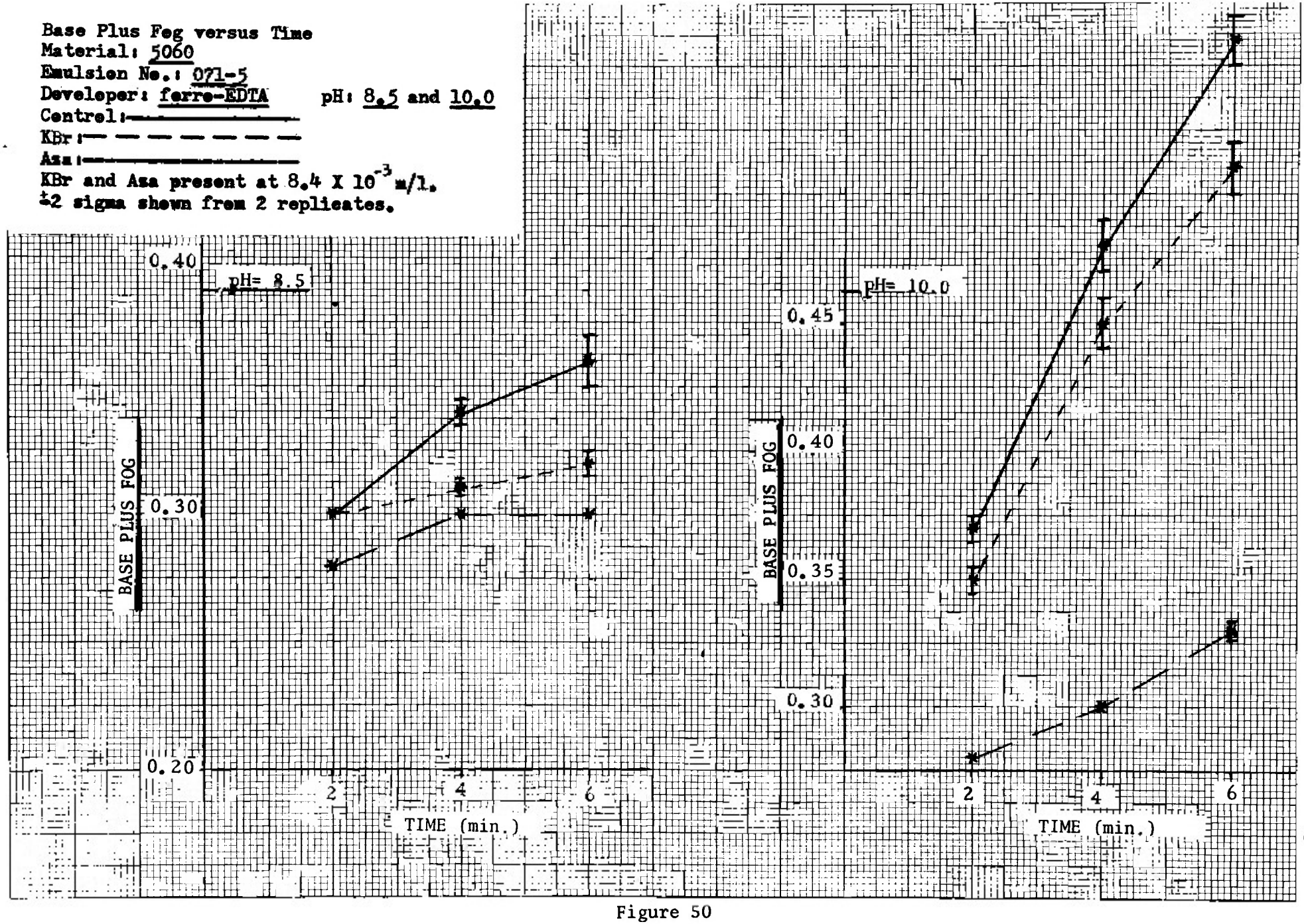

Base Plus Feg versus Time
Material: 5060
Emulsion No.: 071-5
Developer: ferro-EDTA pH: 8.5 and 10.0
Control:
KBr:
Asa:
KBr and Asa present at 8.4 X 10^-3 m/l.
±2 sigma shown from 2 replicates.
pH= 8.5
pH= 10.0
BASE PLUS FOG
0.40
0.30
0.20
0.45
0.35
2
4
6
TIME (min.)

Figure 50

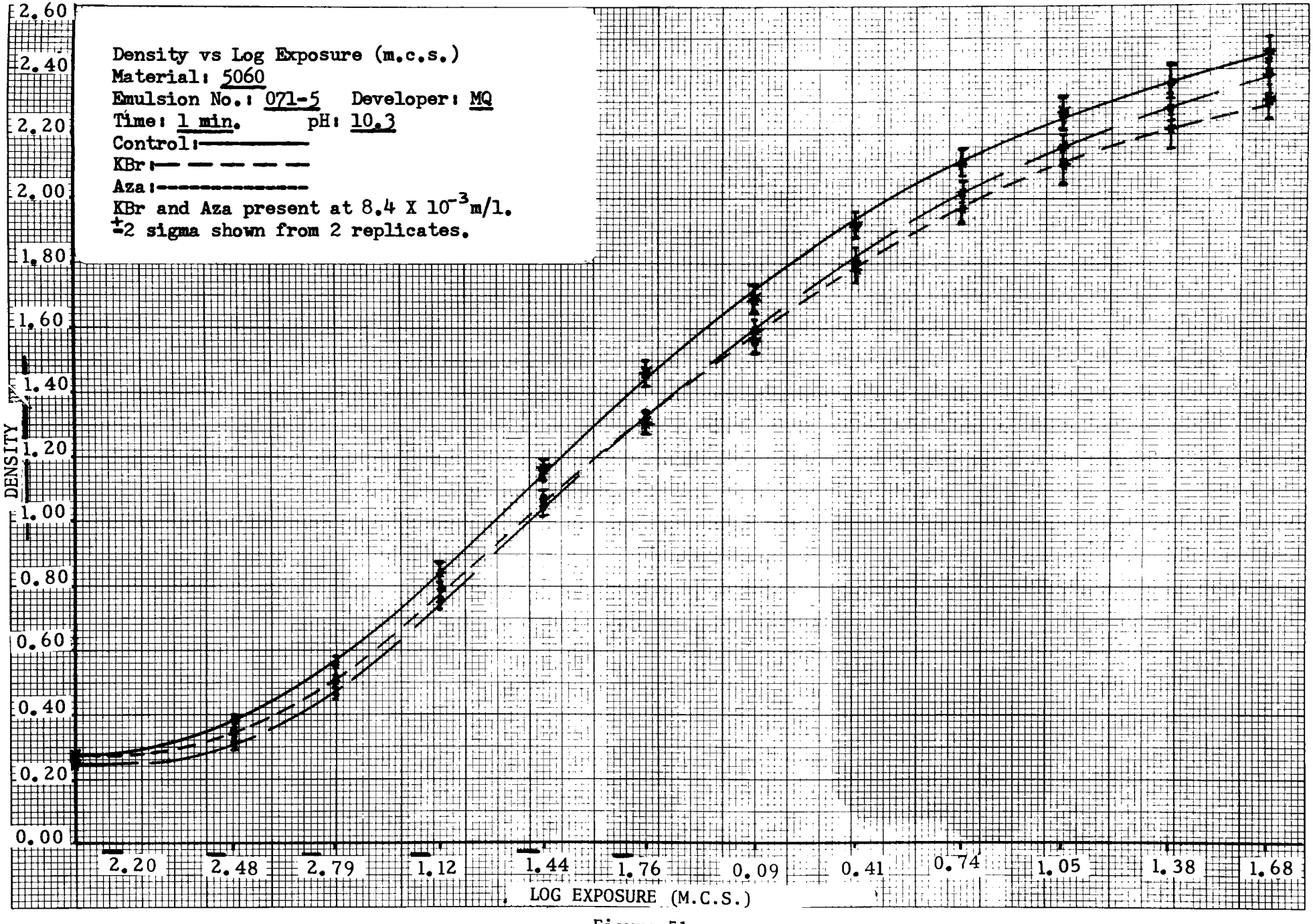

Density vs Log Exposure (m.c.s.)
Material: 5060
Emulsion No.: 071-5 Developer: MQ
Time: 1 min. pH: 10.3
Control:
KBr:
Aza:
KBr and Aza present at 8.4 X 10^{-3}m/l.
±2 sigma shown from 2 replicates.
DENSITY
2.60
2.40
2.20
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
2.20
2.48
2.79
1.12
1.44
1.76
0.09
0.41
0.74
1.05
1.38
1.68
LOG EXPOSURE (M.C.S.)

Figure 51

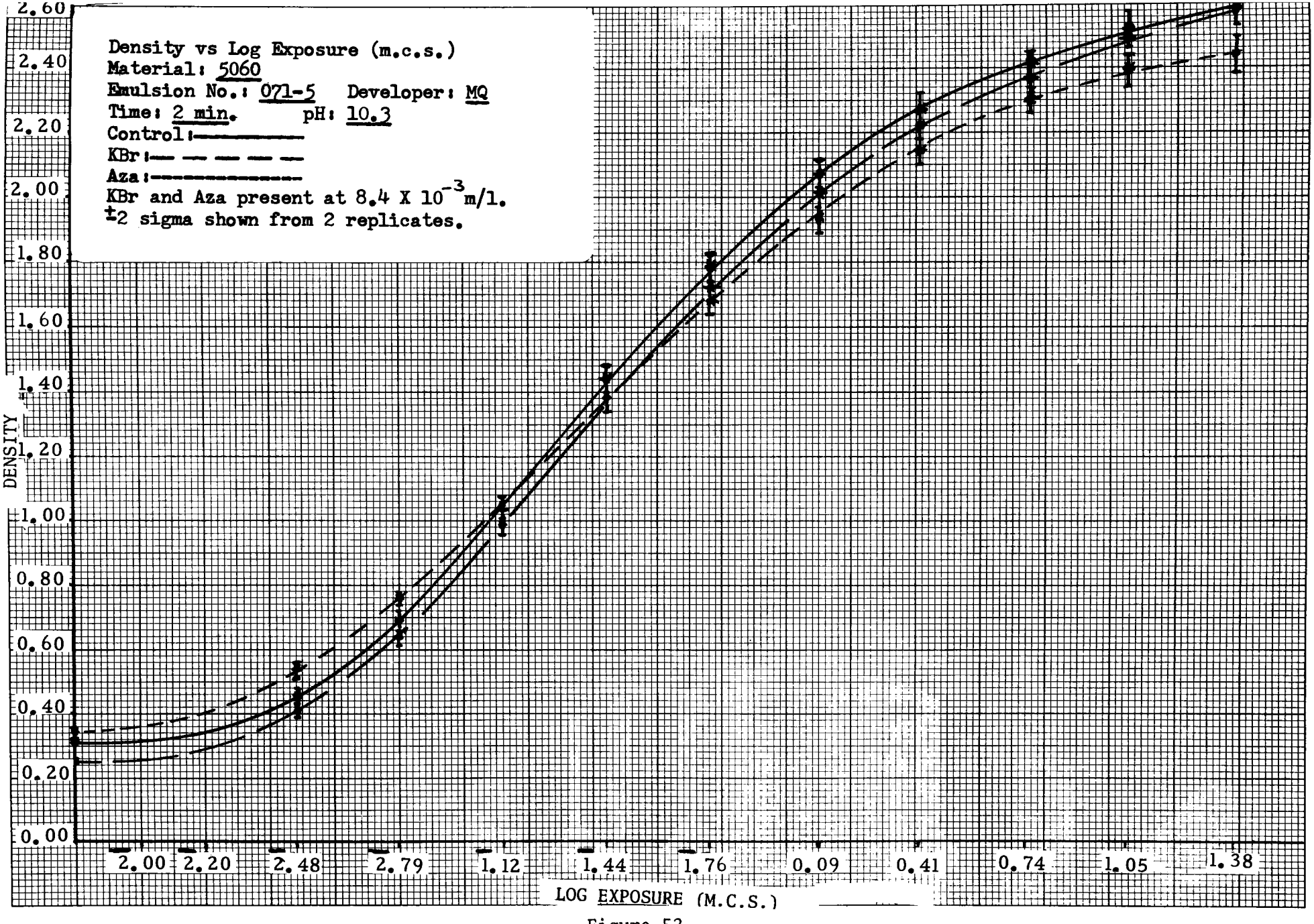

Density vs Log Exposure (m.c.s.)
Material: 5060
Emulsion No.: 071-5 Developer: MQ
Time: 2 min. pH: 10.3
Control:
KBr:
Aza:
KBr and Aza present at 8.4 X 10^-3 m/l.
±2 sigma shown from 2 replicates.
DENSITY
2.60
2.40
2.20
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
2.00
2.20
2.48
2.79
1.12
1.44
1.76
0.09
0.41
0.74
1.05
1.38
LOG EXPOSURE (M.C.S.)

Figure 52

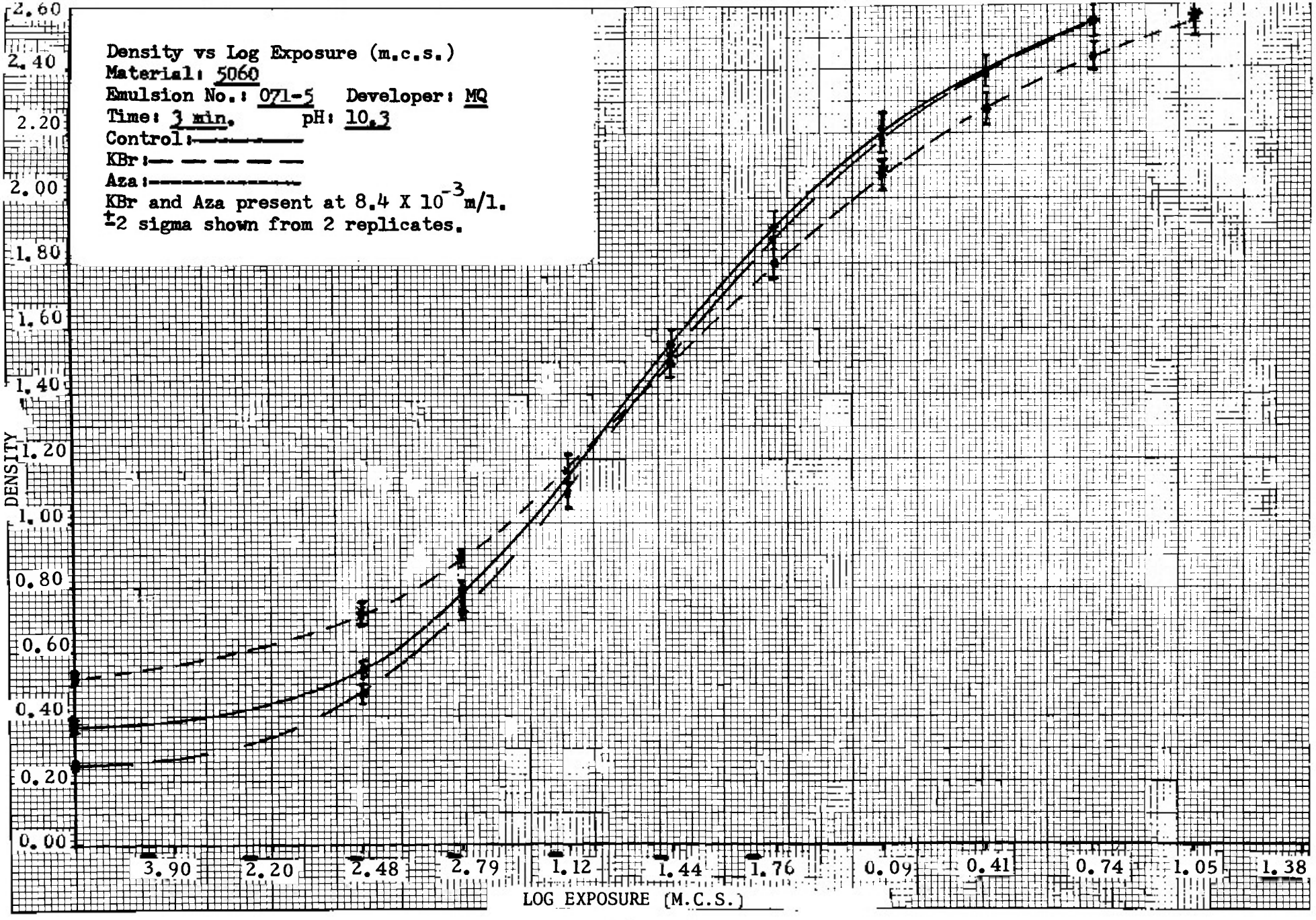

Density vs Log Exposure (m.c.s.)
Material: 5060
Emulsion No.: 071-5 Developer: MQ
Time: 3 min. pH: 10.3
Control:
KBr:
Aza:
KBr and Aza present at 8.4 X 10^-3 m/l.
±2 sigma shown from 2 replicates.
DENSITY
2.60
2.40
2.20
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
3.90
2.20
2.48
2.79
1.12
1.44
1.76
0.09
0.41
0.74
1.05
1.38
LOG EXPOSURE (M.C.S.)

Figure 53

Contrast Index, Exposure Index, and Base Plus Fog versus Time
Material: 5060
Emulsion No.: 071-5
Developer: MQ pH: 10.3
Control:————————
KBr:— — — — —
Aza:----------
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

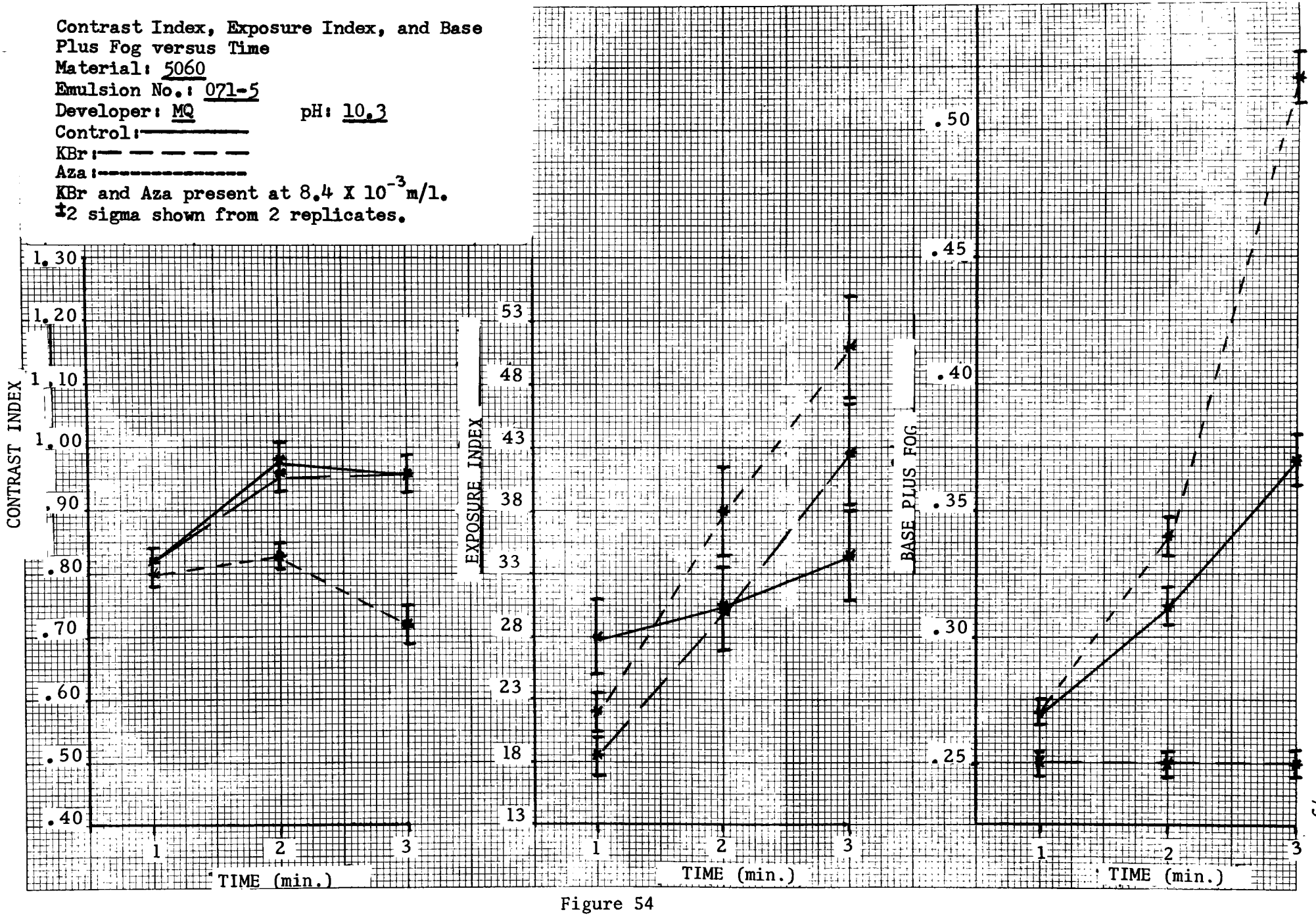


Figure 54

Figure 50 shows the fog suppression of Aza and KBr at pH values 8.5 and 10.0. Even through Aza suppressed fog at pH 10.0 it was much less effective than at 8.5 when compared to KBr.

Since Aza continued to suppress fog at pH 10.0 on the 5060 film and not accelerate if as before on the 5302 film, a check was made to determine if Aza behaved any differently on the 5060 film in the presence of an ordinary MQ developer at high pH. The stock solution of the developer consisted of 4 grams Elon, 90 grams sodium sulfite, 16 grams hydroquinone, 160 grams sodium carbonate, and distilled water to 1 liter. The control solution was obtained by diluting the stock solution 1:1 with distilled water. Aza and KBr were added at 8.4×10^{-3} m/l as before. The pH was maintained at 10.3. The results are shown on Figures 51 through 54.

Even though Aza reduced the higher densities more than KBr as before, it accelerated both speed and fog formation of the 5060 film in the MQ developer at pH 10.3.

Concentration Study

Because both pH and concentration have been reported to influence the activity of Aza, a concentration series was run with pH held at a constant 7.0, (chosen as a representative emulsion pH).

5302 Processed in Amidol. Three different levels of concentration of Aza were tested, (i.e. 8.4×10^{-3}, 3.78×10^{-2}, and 8.4×10^{-2} m/l). Development times were 2, 4, and 6 minutes. Processing conditions were the same as previously described for the Amidol-5302 combination. Results: Figures 55 through 58 indicate the results of these tests.

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 183-531
Developer: Amidol Time: 2 min. pH: 7.0
Control: ——————————
Aza at 8.40 X 10^{-3} m/l: ••••••••••••••••••
Aza at 3.78 X 10^{-2} m/l: — — — — — — — —
Aza at 8.40 X 10^{-2} m/l: — — — — — — — —
±2 sigma shown from 2 replicates.

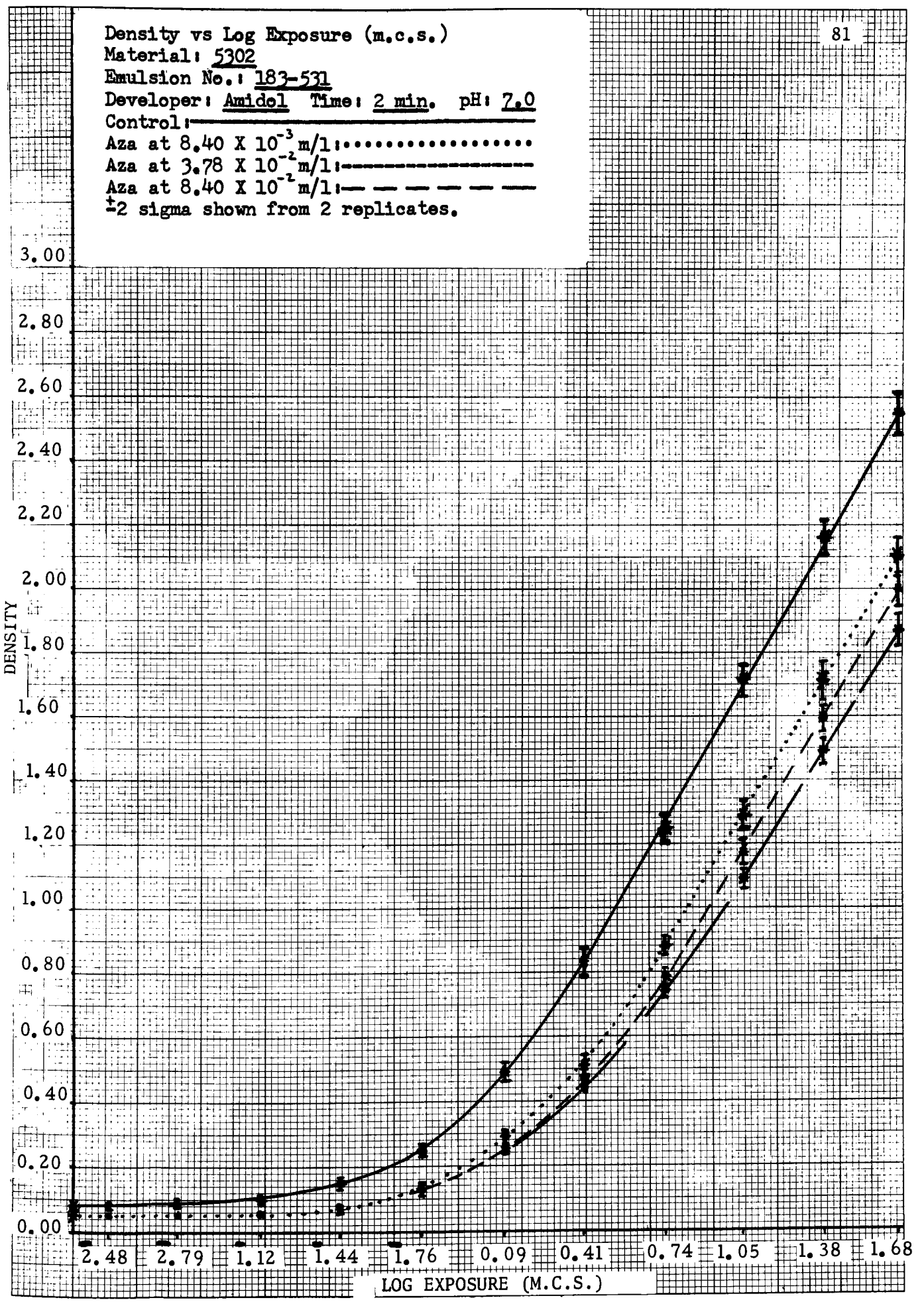


Figure 55

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 183-531
Developer: Amidol: Time: 4 min. pH: 7.0
Control: ——————————
Aza at 8.40 X 10^{-3} m/l: ·····
Aza at 3.78 X 10^{-2} m/l: - - - - - -
Aza at 8.40 X 10^{-2} m/l: — — — — — —
±2 sigma shown from 2 replicates.

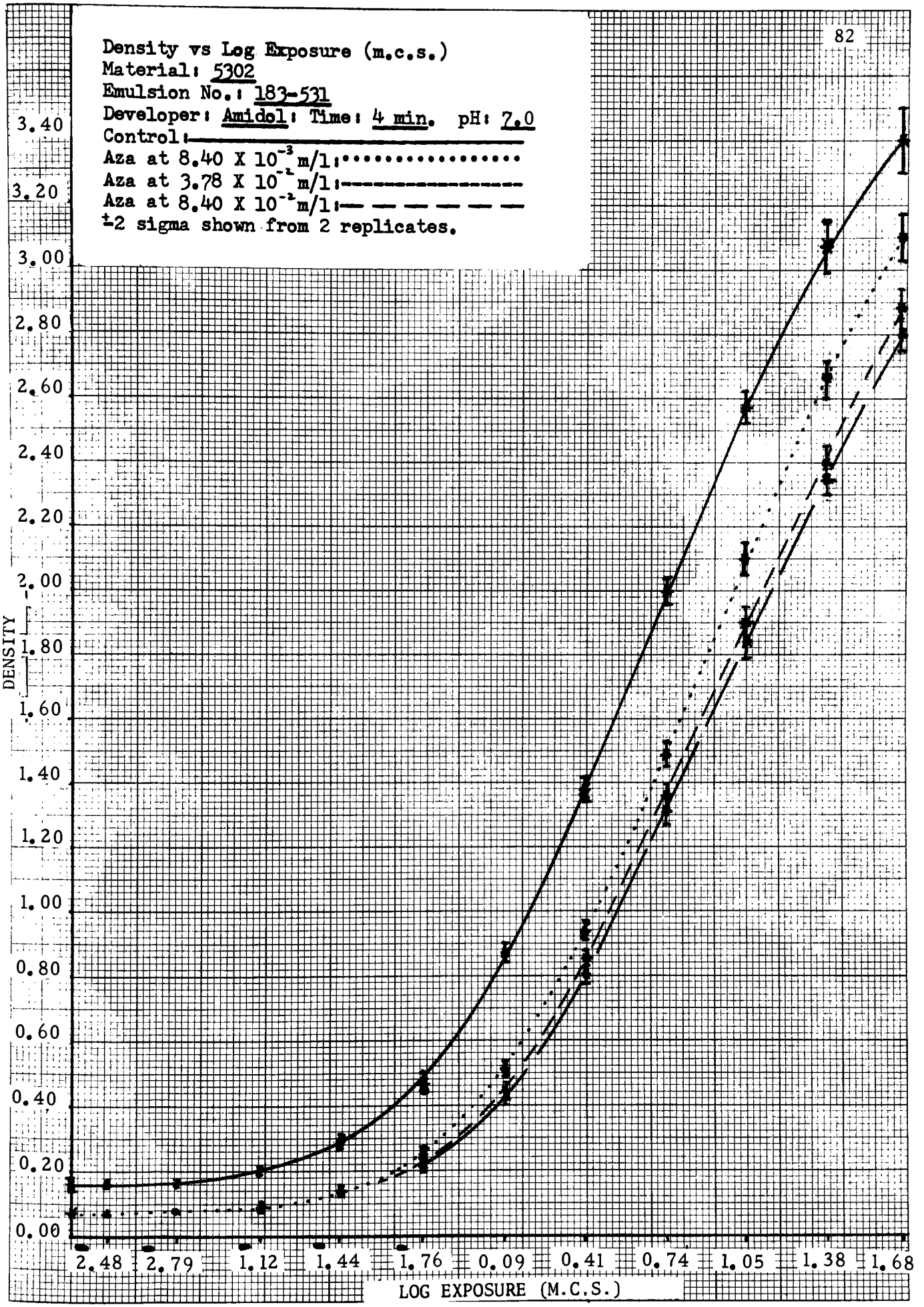


Figure 56

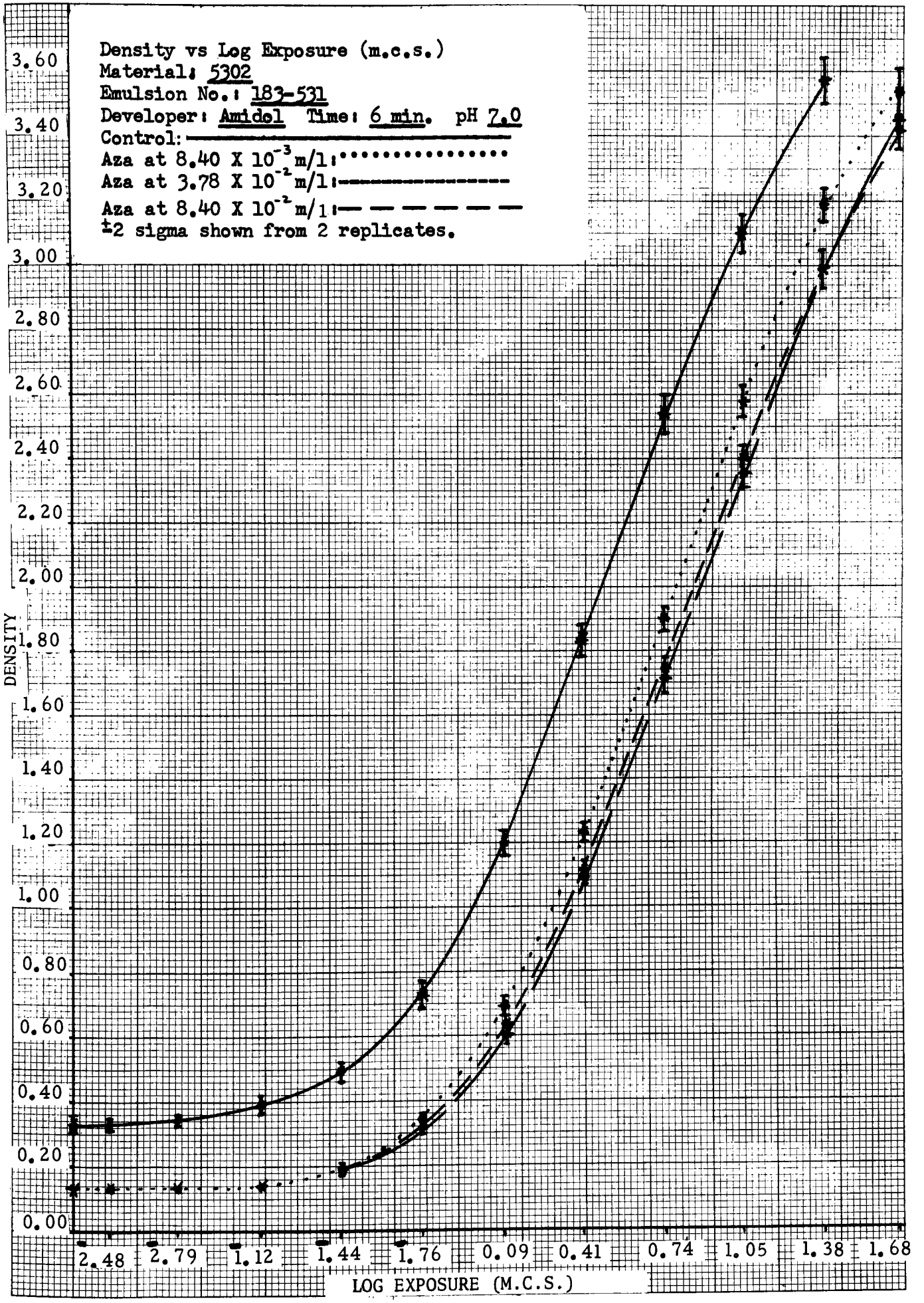

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 183-531
Developer: Amidol Time: 6 min. pH 7.0
Control:
Aza at 8.40 X 10⁻³ m/l:
Aza at 3.78 X 10⁻² m/l:
Aza at 8.40 X 10⁻² m/l:
±2 sigma shown from 2 replicates.
DENSITY
3.60
3.40
3.20
3.00
2.80
2.60
2.40
2.20
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
2.48
2.79
1.12
1.44
1.76
0.09
0.41
0.74
1.05
1.38
1.68
LOG EXPOSURE (M.C.S.)

Figure 57

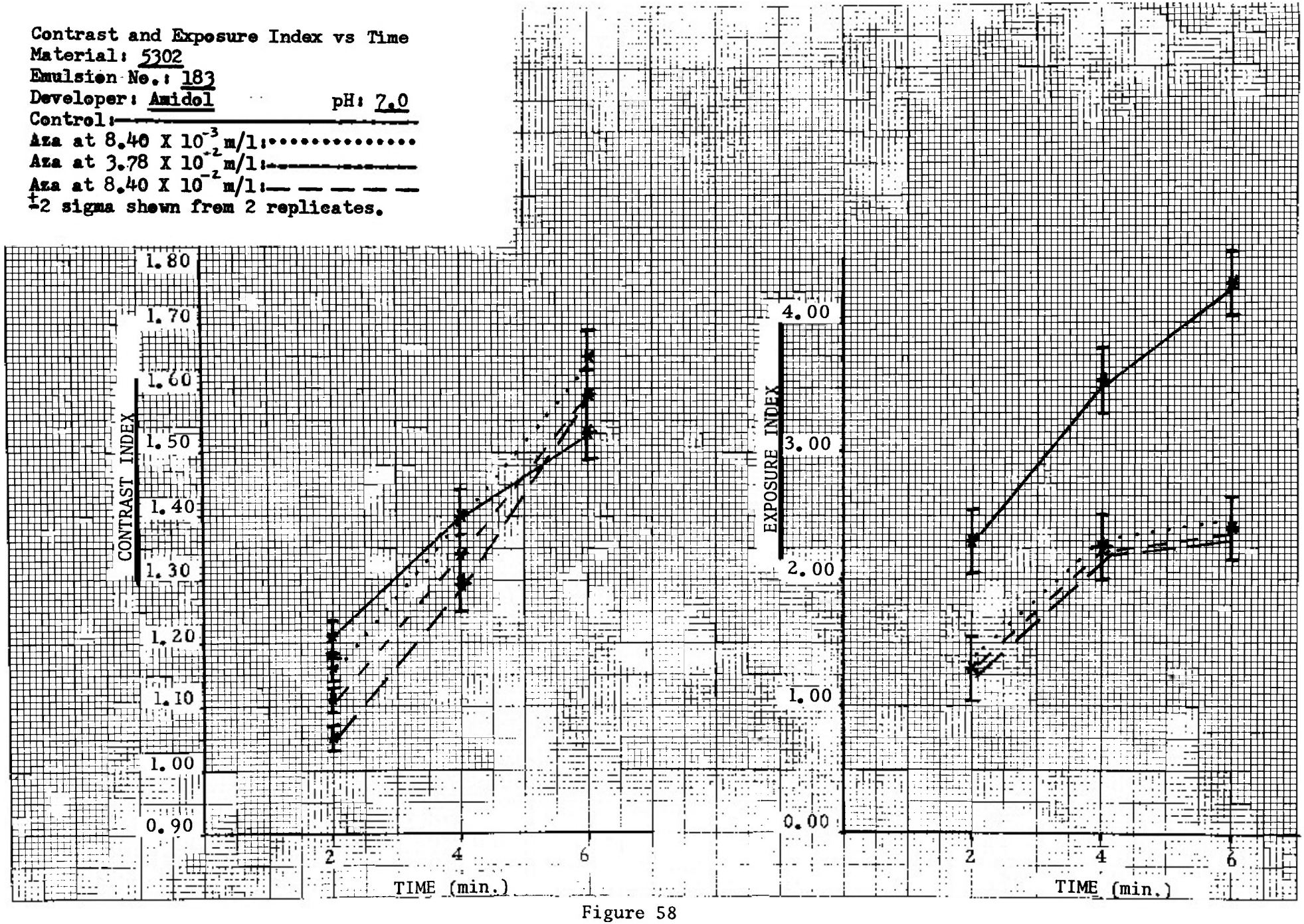

Contrast and Exposure Index vs Time
Material: 5302
Emulsion No.: 183
Developer: Amidol pH: 7.0
Control:
Aza at 8.40 X 10^-3 m/l:
Aza at 3.78 X 10^-2 m/l:
Aza at 8.40 X 10^-2 m/l:
±2 sigma shown from 2 replicates.
CONTRAST INDEX
1.80
1.70
1.60
1.50
1.40
1.30
1.20
1.10
1.00
0.90
EXPOSURE INDEX
4.00
3.00
2.00
1.00
0.00
2
4
6
TIME (min.)
2
4
6
TIME (min.)

Figure 58

The three levels of Aza all had the same effect on speed and fog. As the concentration was increased the contrast index decreased for the 2 minute development. Aza at 8.4×10^{-2} m/l was not significantly different from the 3.78×10^{-2} m/l level for 4 and 6 minutes of development.

5302 Processed in Fe-EDTA. With the pH maintained at 7.0 the following concentrations of Aza and KBr were studied: 8.4×10^{-4}, 3.78×10^{-3}, 8.4×10^{-3}, 3.78×10^{-2}, and 8.4×10^{-2} m/l. The processing conditions were the same as before with times of 4, 7, and 10 minutes.

Results: Figures 59 through 61 are the results of Aza and KBr at 8.4×10^{4} m/l, Figures 62 through 64 at 3.78×10^{-3} m/l, Figures 65 through 67 at 8.4×10^{-3} m/l, Figures 68 through 70 at 3.78×10^{-2} m/l, and Figures 71 through 73 at 8.4×10^{-2} m/l. Figure 74 shows contrast and exposure index versus time curves for control and various levels of Aza concentration.

The data for the concentration series indicate that at high concentrations in the Fe-EDTA, Aza no longer restrained development. In some cases the higher concentrations even accelerated the rate of development and the formation of fog. No explanation for the existence of an optimum concentration of Aza in Fe-EDTA is possible on the available evidence; this was not observed in the Amidol developer at the same pH. In contrast to Aza, KBr restrained development more when present in high concentrations.

5060 Film Processed in Fe-EDTA. Two levels of Aza were tested here, (i.e. 8.4×10^{-3} and 8.4×10^{-2} m/l). Processing conditions were the same as before with times of 2 and 6 minutes. Results: Figures 75 through 77 show the effects.

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 4 min. pH: 7.0
Control:————————
KBr:— — — — —
Aza:——————————
KBr and Aza present at 8.4×10^{-4} m/l.
±2 sigma shown from 2 replicates.

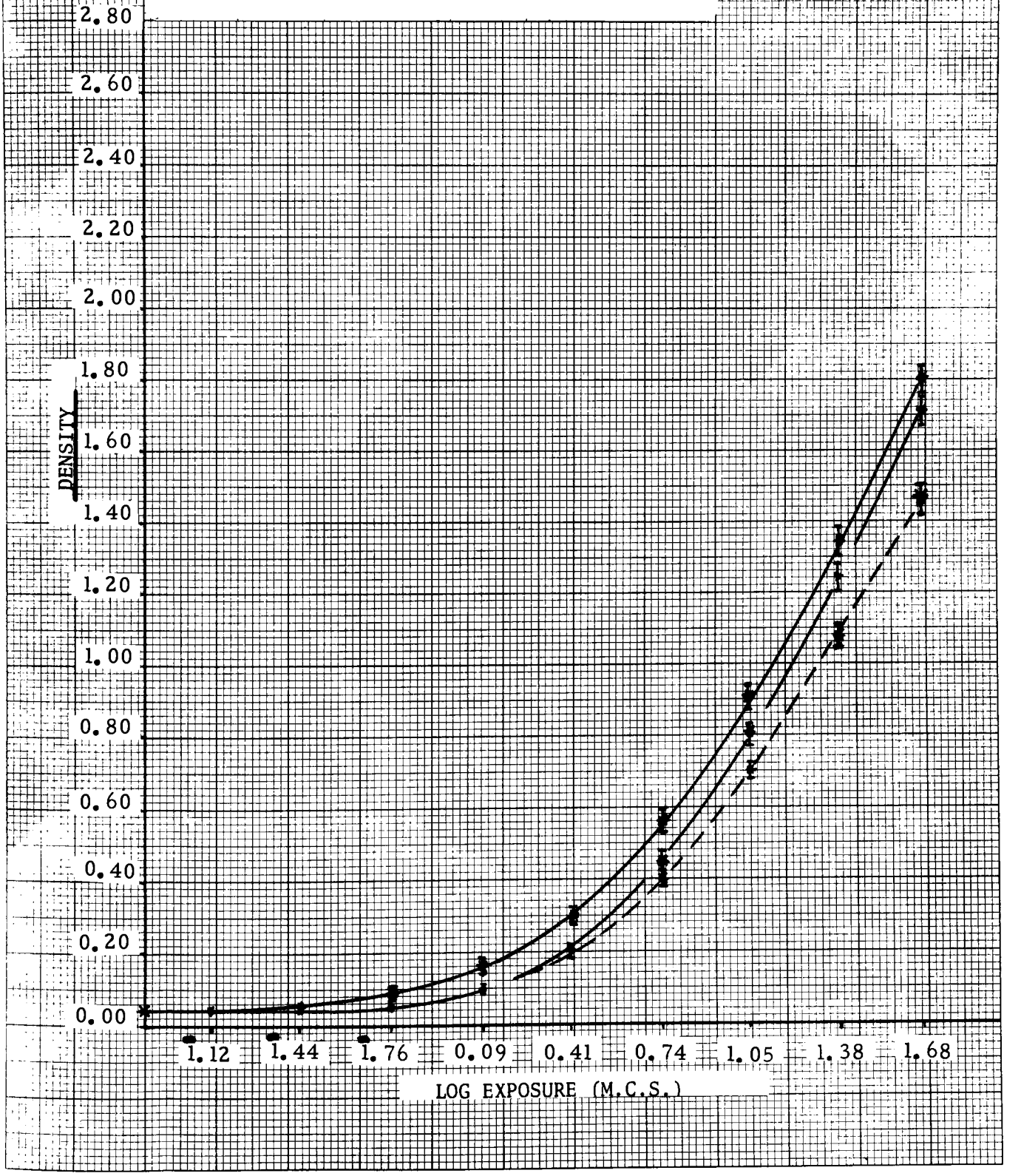


Figure 59

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 7 min. pH: 7.0
Control:————————
KBr:— — — — —
Aza:- - - - - - - - -
KBr and Aza present at 8.4×10^{-4} m/l.
±2 sigma shown from 2 replicates.

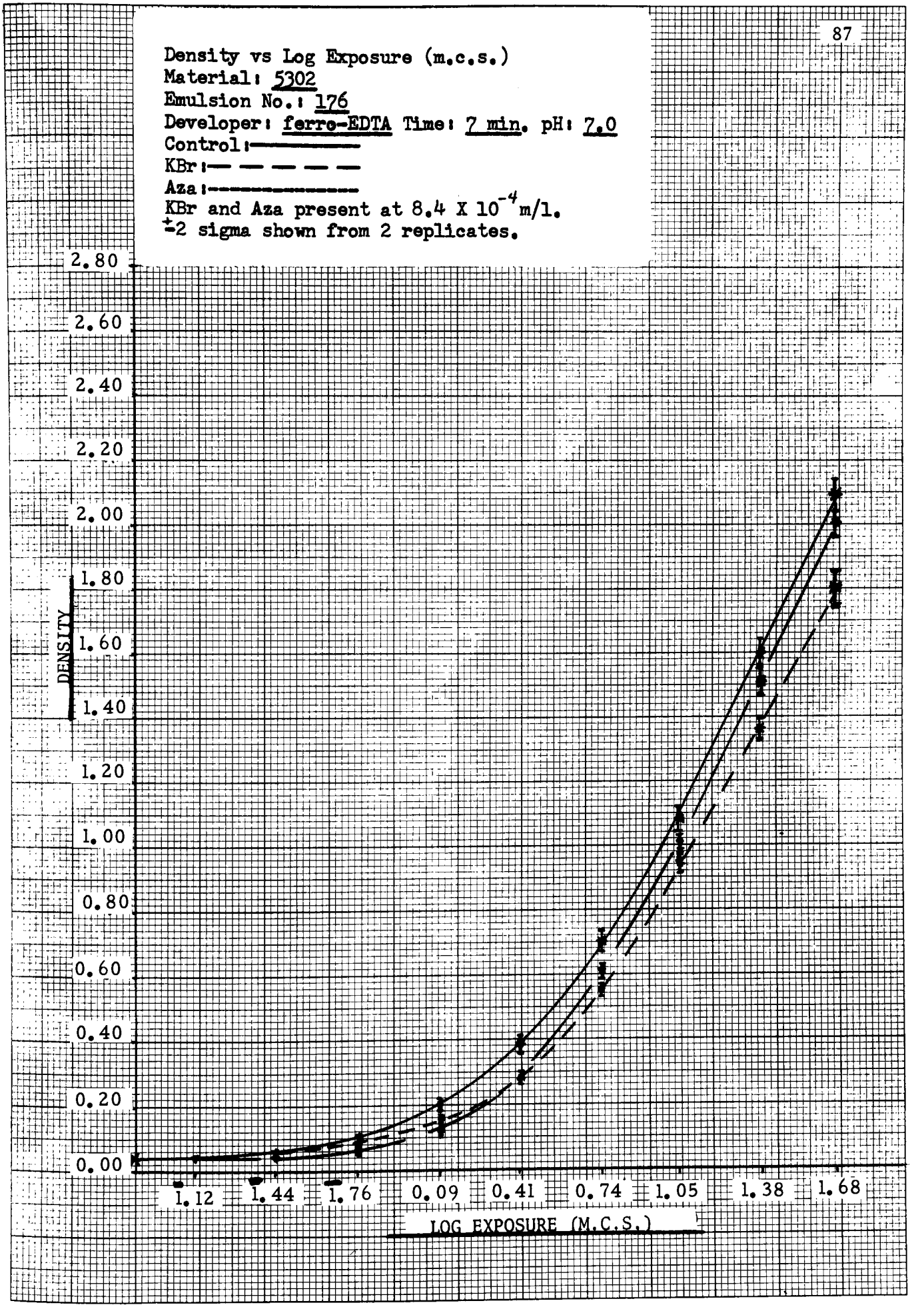


Figure 60

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 10 min. pH: 7.0
Control: ——————
KBr: — — — — —
Aza: ——————
KBr and Aza present at 8.4×10^{-4} m/l.
±2 sigma shown from 2 replicates.

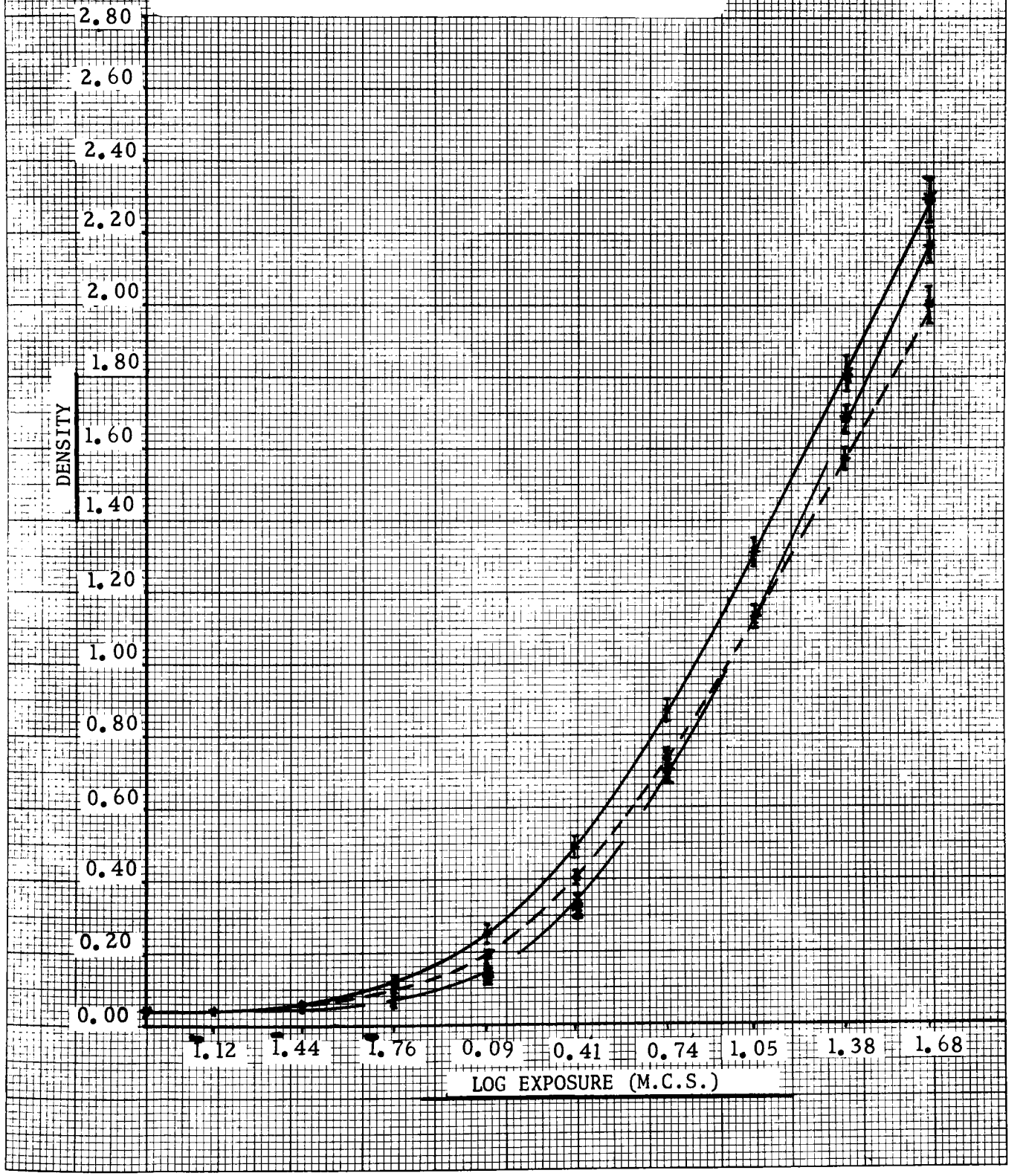


Figure 61

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 4 min. pH: 7.0
Control: ————————
KBr: — — — — —
Aza: ————————
KBr and Aza present at 3.78×10^{-3} m/l.
± 2 sigma shown from 2 replicates.

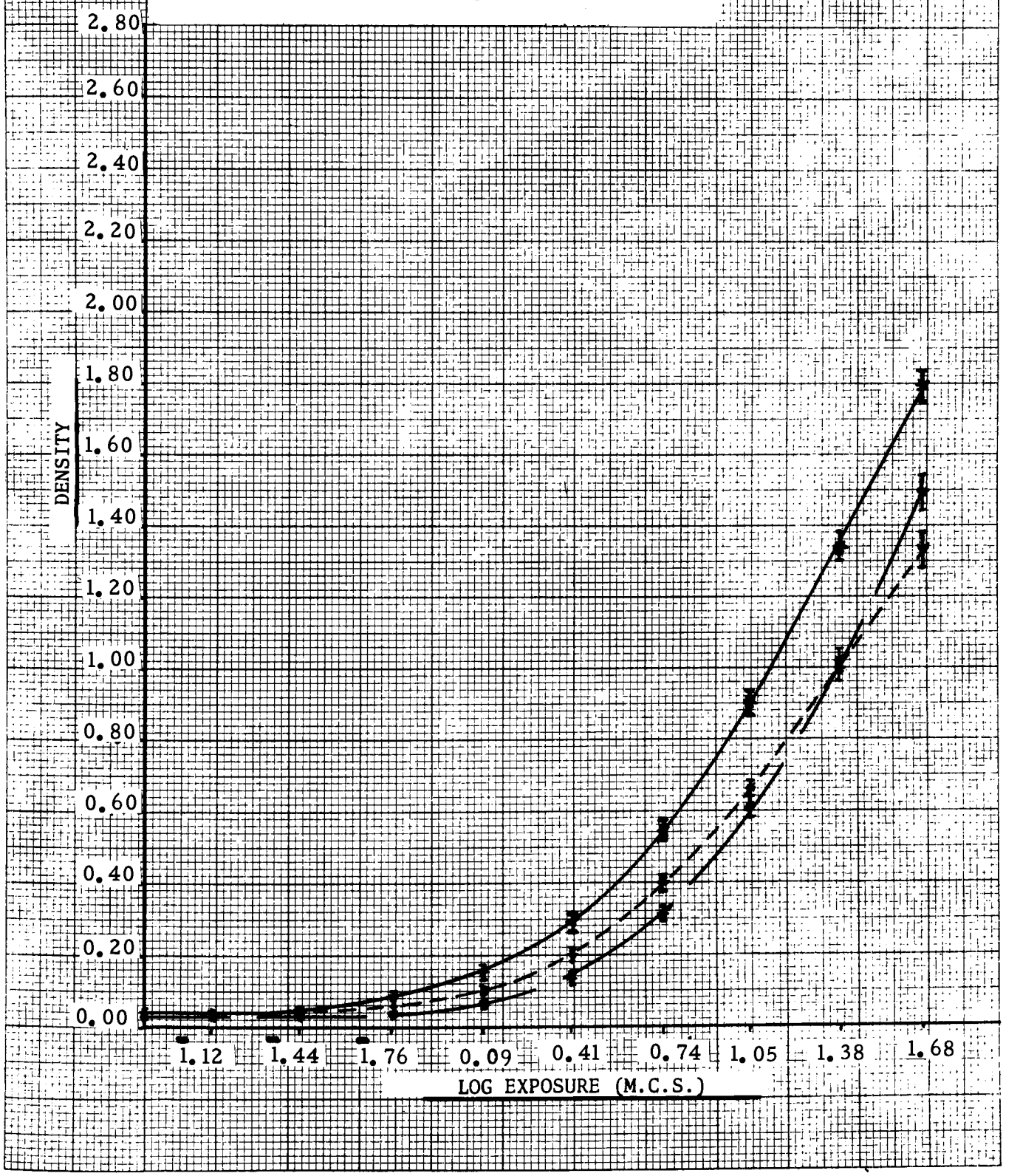


Figure 62

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 7 min. pH: 7.0
Control:————
KBr:— — — —
Aza:- - - - - - -
KBr and Aza present at 3.78×10^{-3} m/l.
±2 sigma shown from 2 replicates.

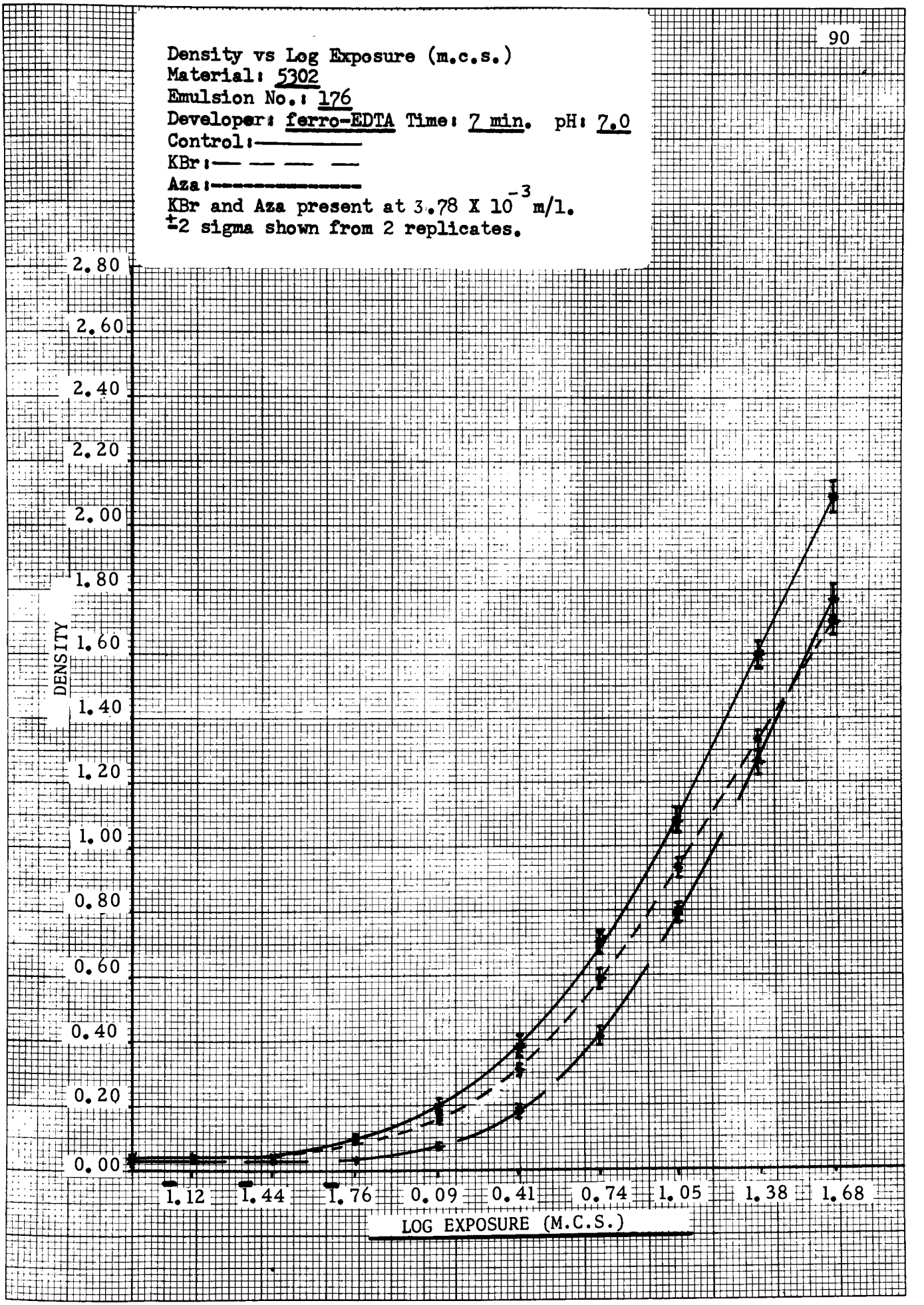


Figure 63

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 10 min. pH: 7.0
Control:————————
KBr: — — — — —
Aza:- - - - - - - - - - - -
KBr and Aza present at 3.78×10^{-3} m/l.
±2 sigma shown from 2 replicates.

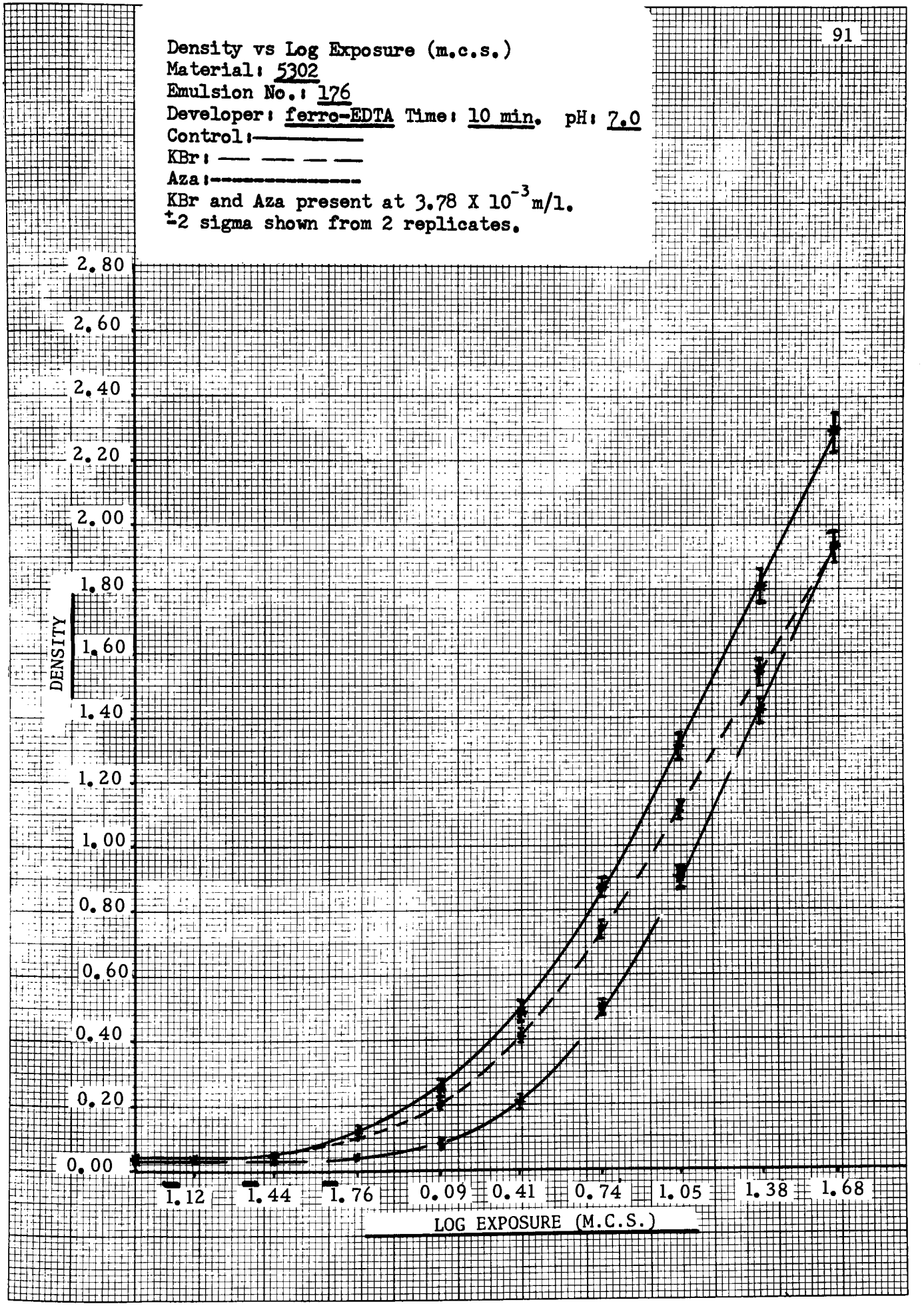


Figure 64

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 4 min. pH: 7.0
Control:————————
KBr:— — — — —
Aza:— — — — — — —
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

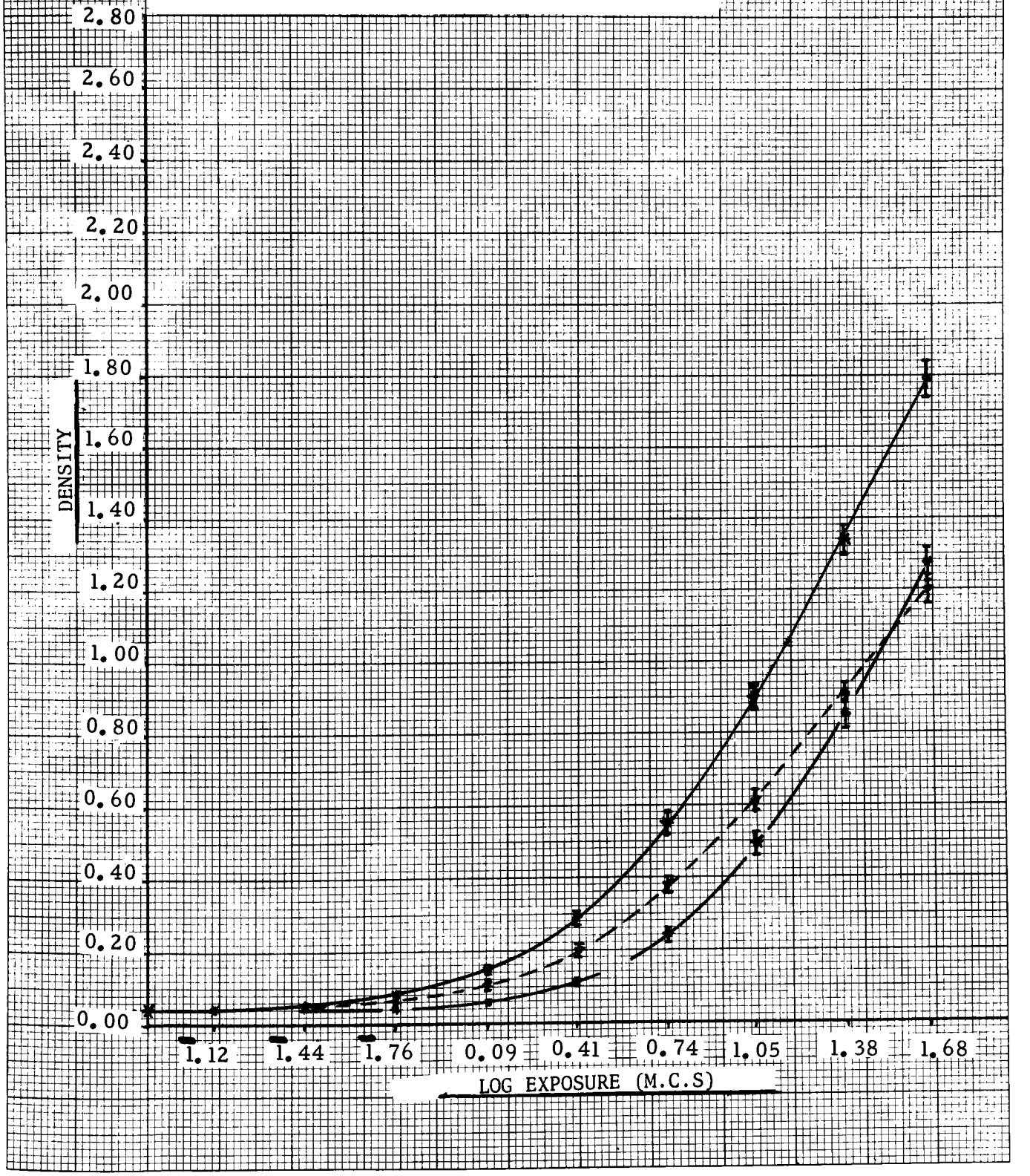


Figure 65

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 7 min. pH: 7.0
Control:————————
KBr:— — — — —
Aza:— — — — — —
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

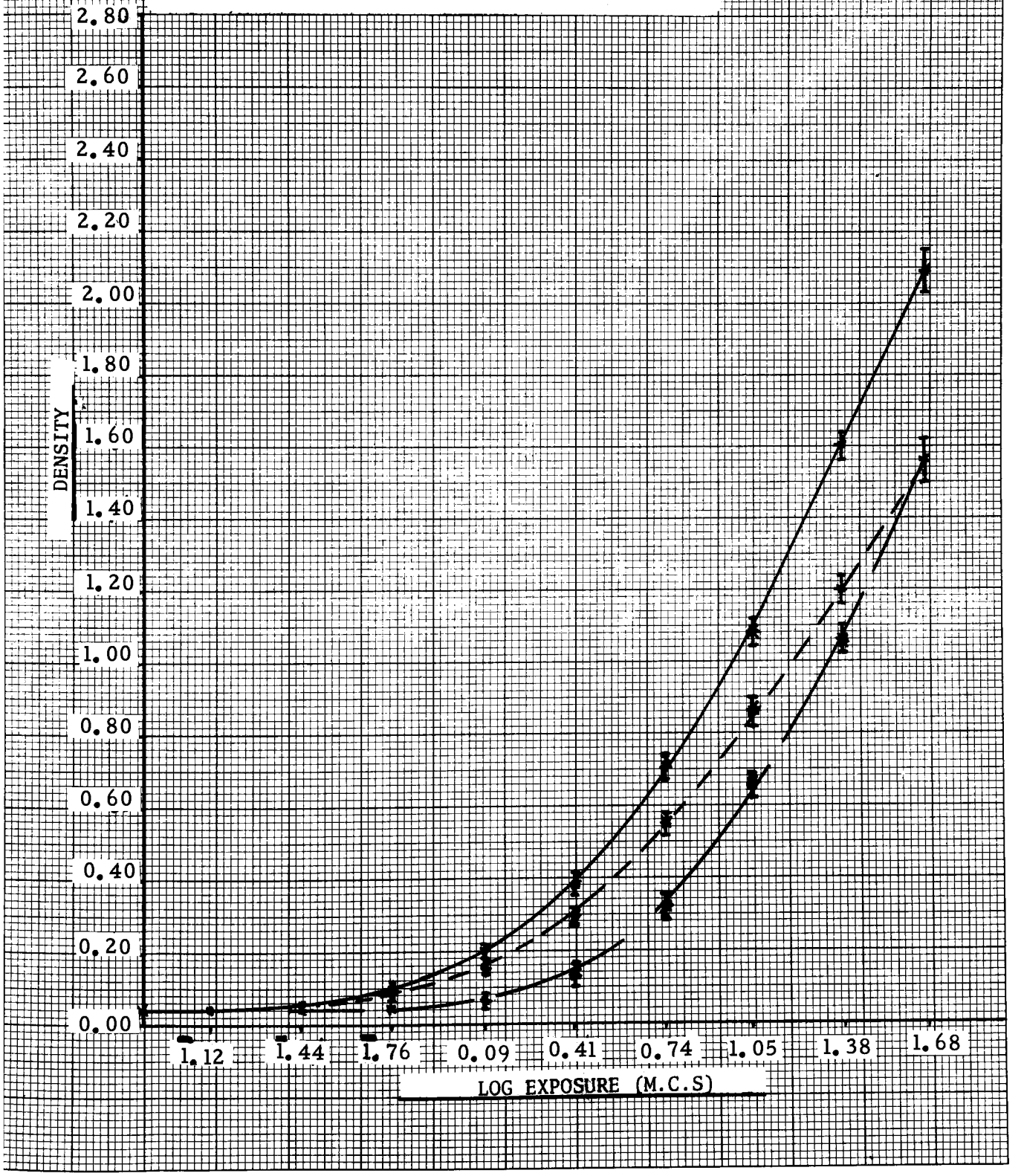


Figure 66

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 10 min. pH: 7.0
Control: ————————
KBr: — — — — —
Aza: ————————
KBr and Aza present at 8.4×10^{-3} m/l.
±2 sigma shown from 2 replicates.

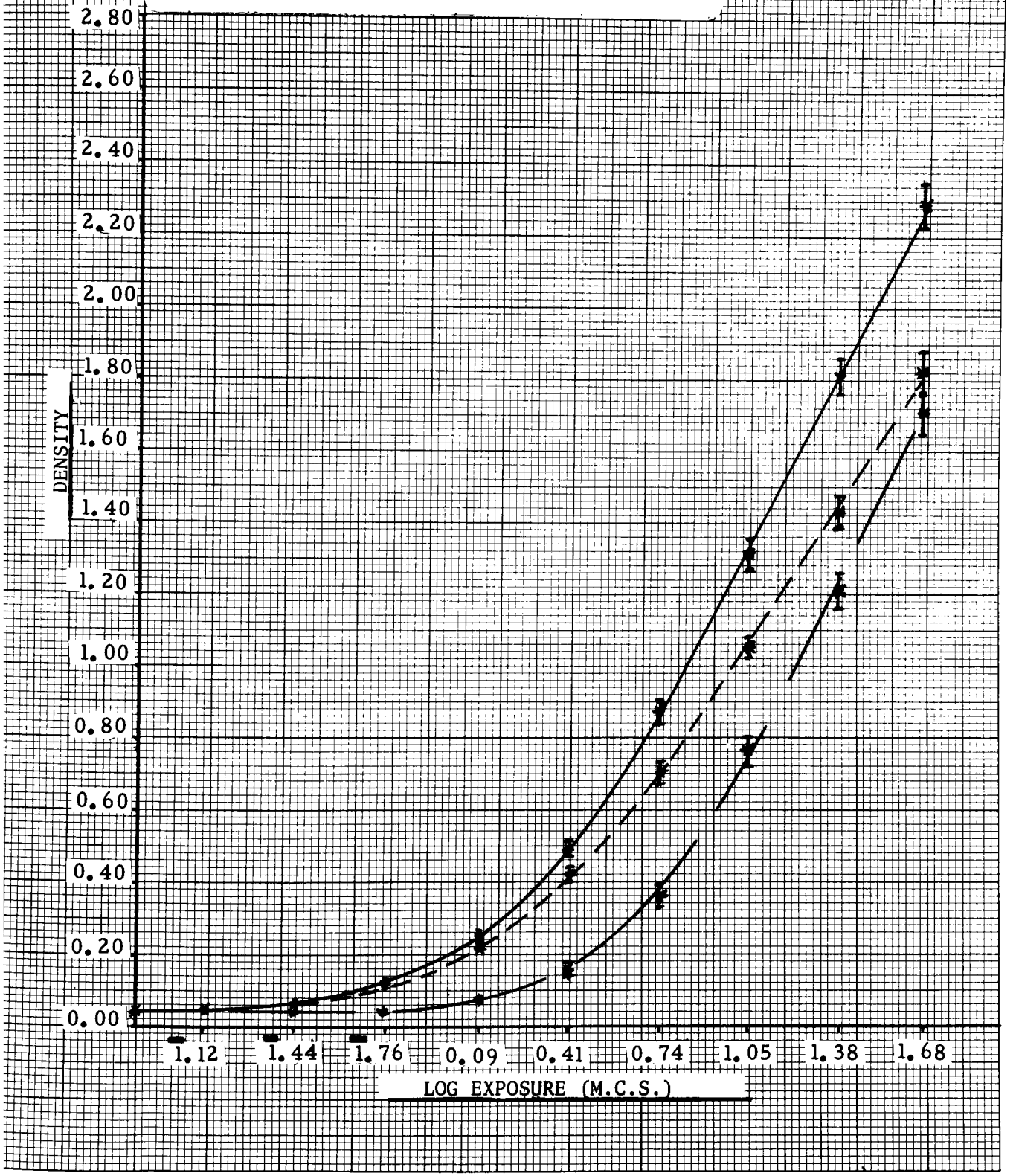


Figure 67

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 4 min. pH: 7.0
Control: ————————
KBr: — — — — —
Aza: ————————
KBr and Aza present at 3.78×10^{-2} m/l.
±2 sigma shown from 2 replicates.

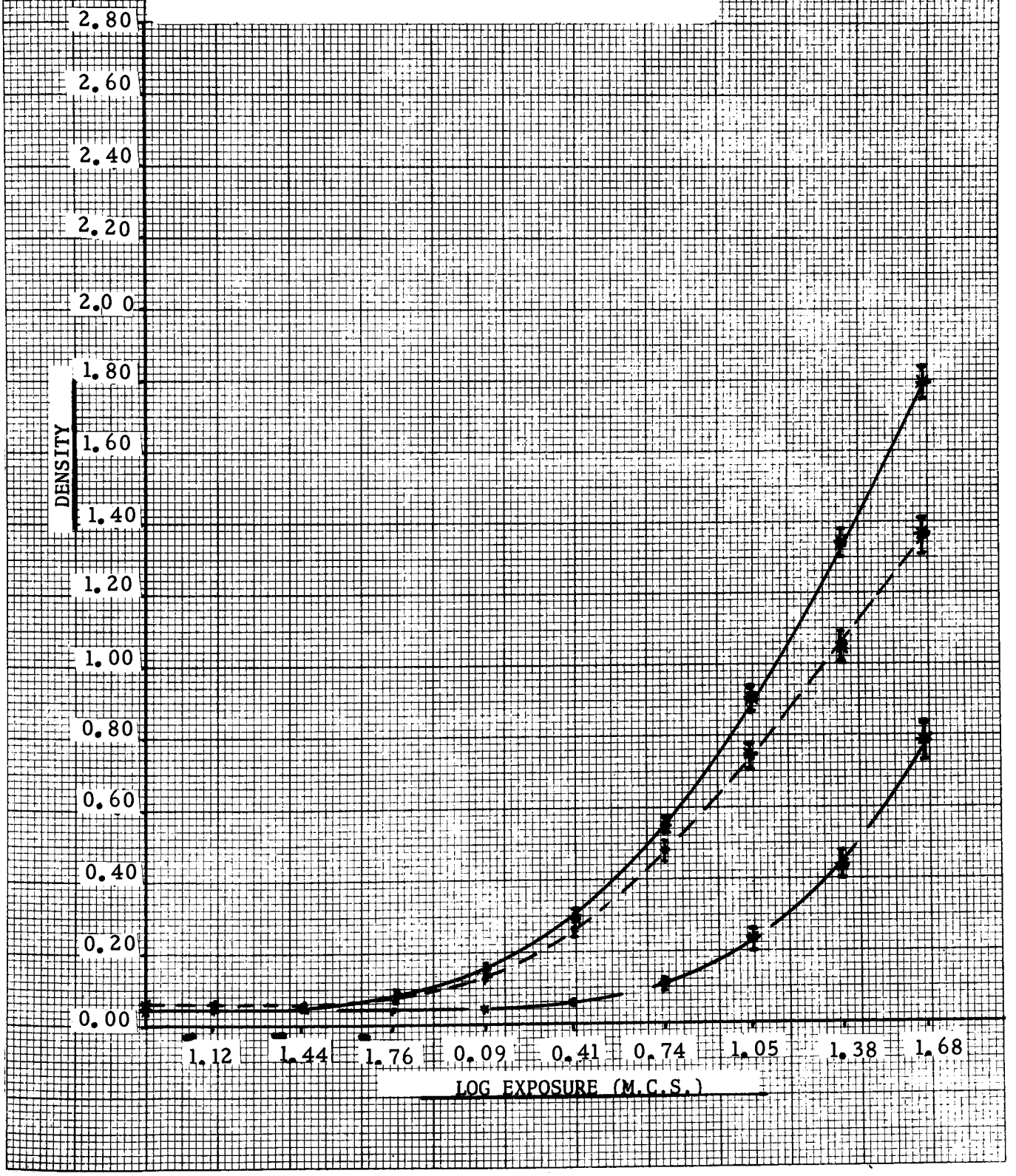


Figure 68

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 7 min. pH: 7.0
Control: ————————
KBr: — — — — —
Aza: ————————
KBr and Aza present at 3.78×10^{-2} m/l.
±2 sigma shown from 2 replicates.

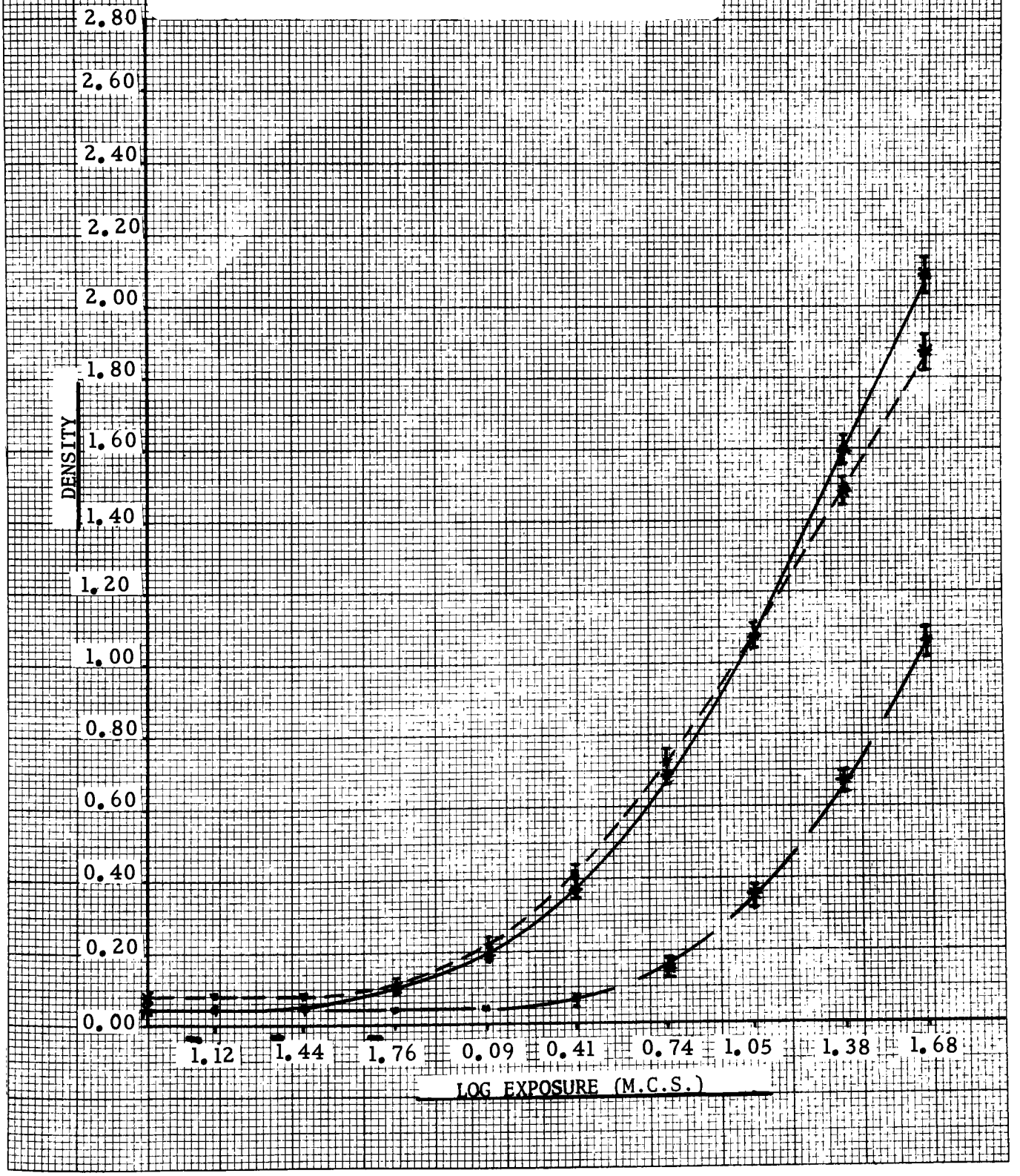


Figure 69

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 10 min. pH: 7.0
Control: ————————
KBr: — — — — —
Aza: ————————
KBr and Aza present at 3.78×10^{-2} m/l.
±2 sigma shown from 2 replicates.

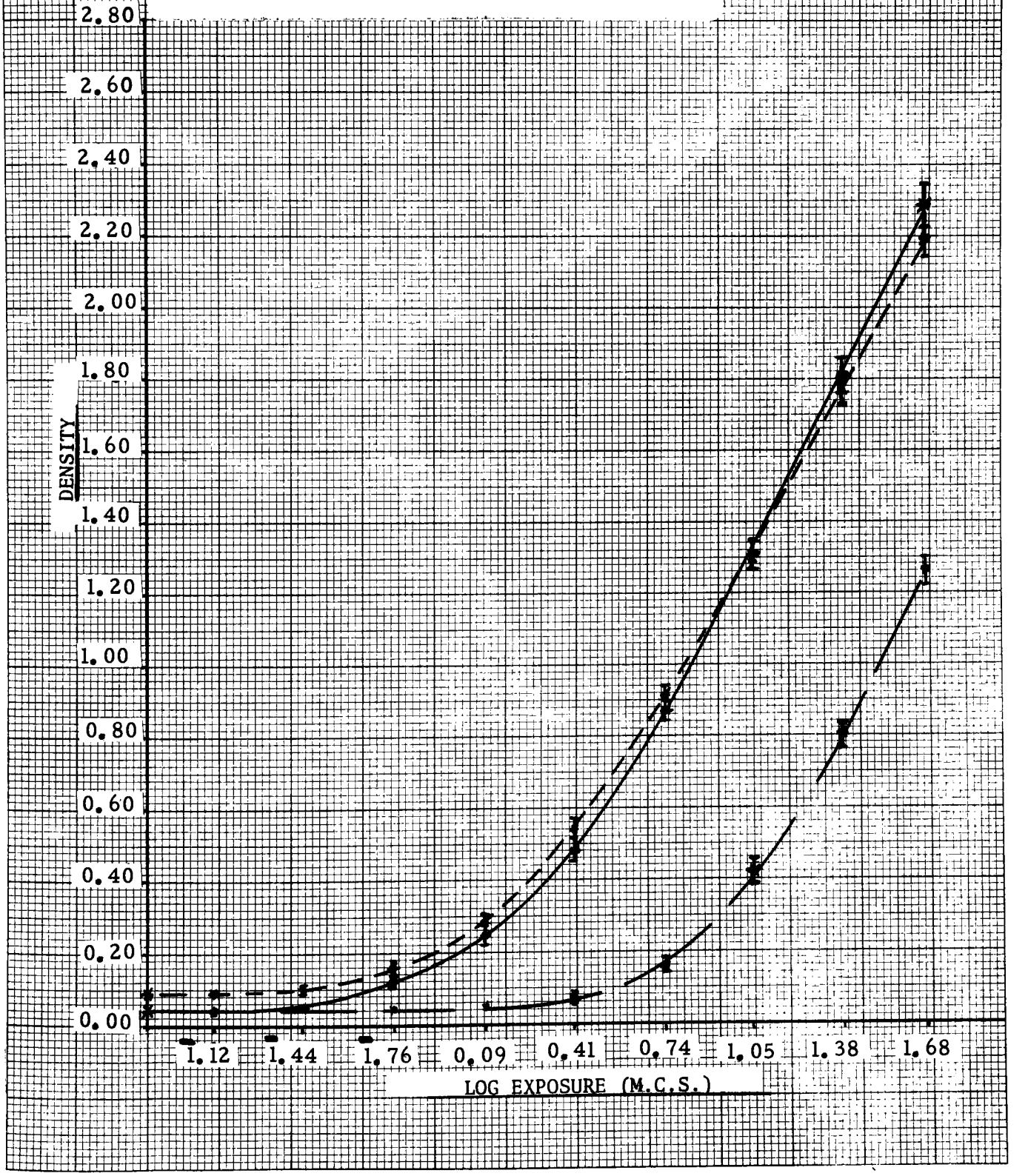


Figure 70

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 4 min. pH: 7.0
Control:————————
KBr:— — — — —
Aza:————————
KBr and Aza present at 8.4×10^{-2} m/l.
±2 sigma shown from 2 replicates.

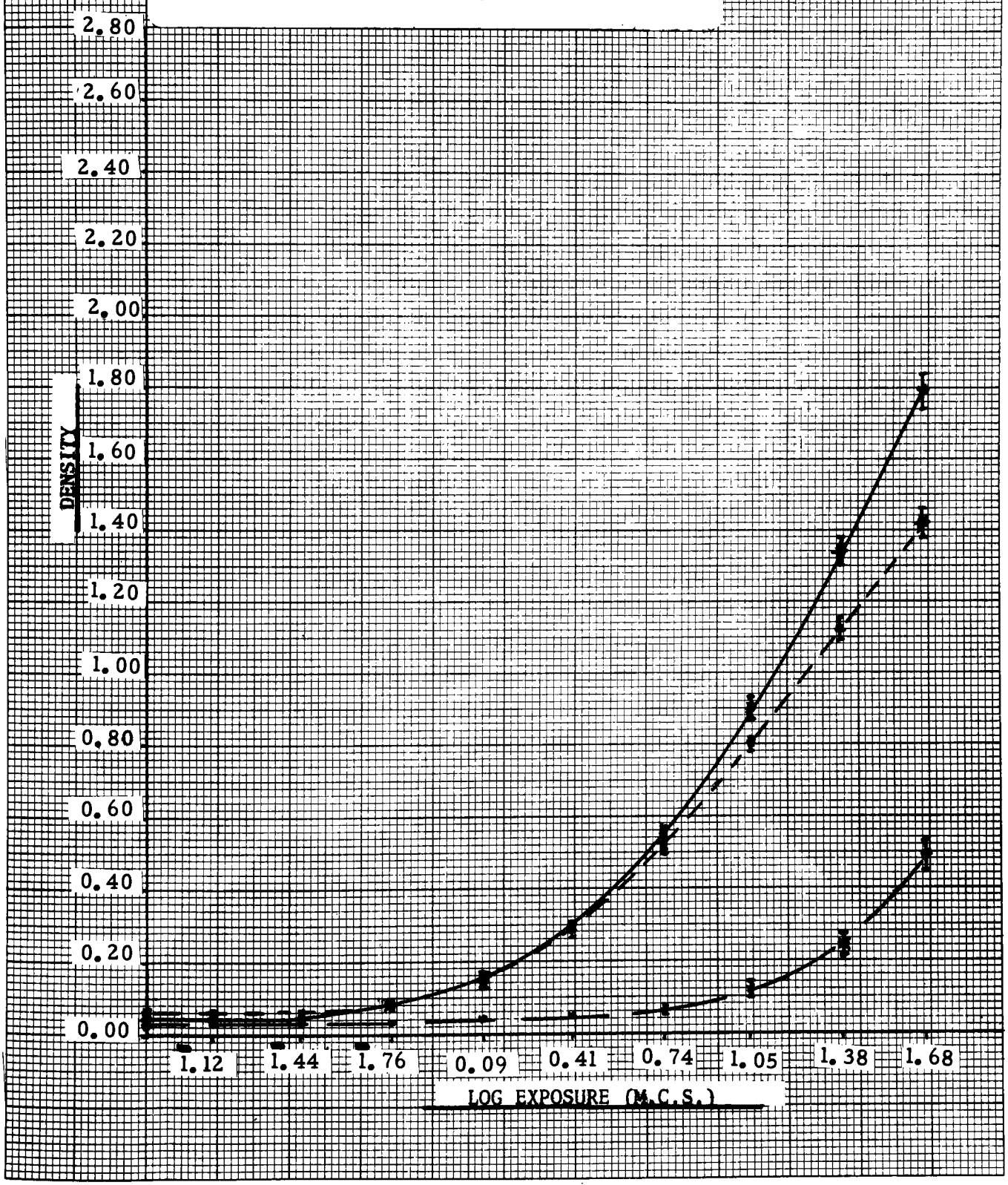


Figure 71

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 7 min. pH: 7.0
Control:————————
KBr:— — — — —
Aza:————————
KBr and Aza present at 8.4×10^{-2} m/l.
±2 sigma shown from 2 replicates.

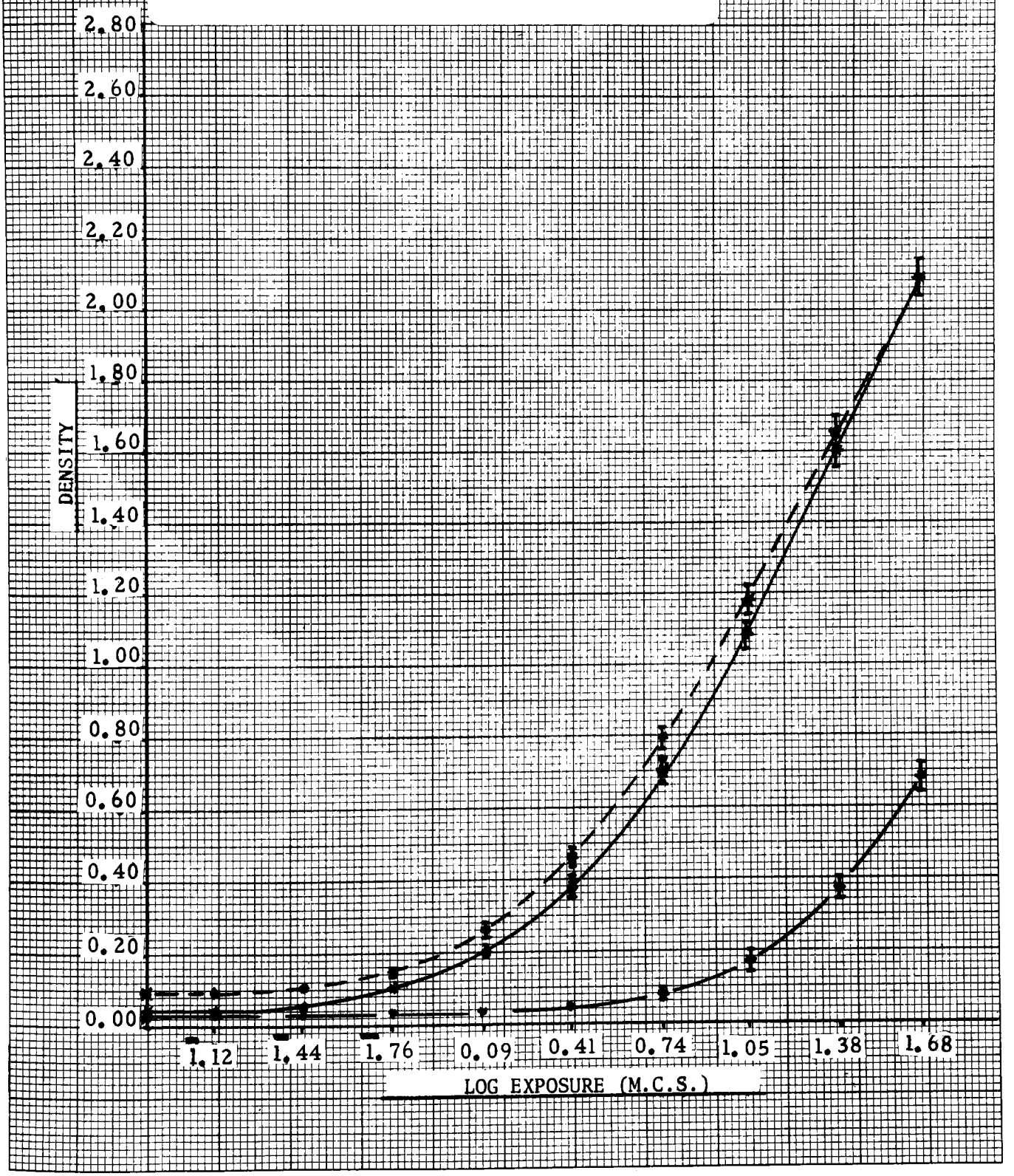


Figure 72

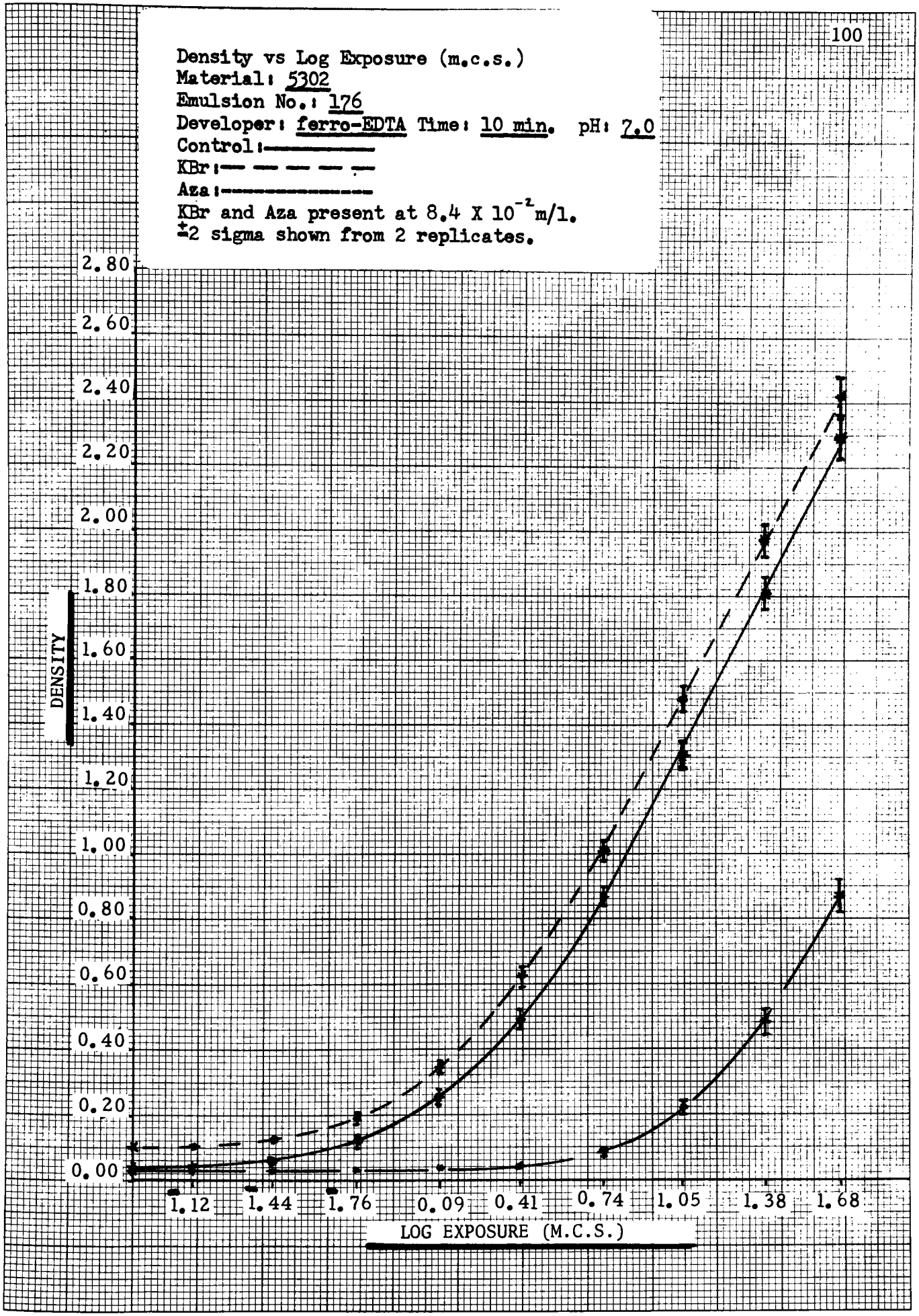

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 10 min. pH: 7.0
Control:
KBr:
Aza:
KBr and Aza present at 8.4 X 10⁻² m/l.
±2 sigma shown from 2 replicates.
100
2.80
2.60
2.40
2.20
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
DENSITY
1.12
1.44
1.76
0.09
0.41
0.74
1.05
1.38
1.68
LOG EXPOSURE (M.C.S.)

Figure 73

Contrast Index versus Time
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA pH: 7.0
Control: ——————
Aza at 8.40×10^{-2} m/l: ••••••••••••••••
Aza at 3.78×10^{-3} m/l: ——————
Aza at 8.40×10^{-3} m/l: — — — — — —
±2 sigma shown from 2 replicates.

Exposure Index versus Time
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA pH: 7.0
Control: ——————
Aza at 8.40×10^{-2} m/l: ••••••••••••••••
Aza at 3.78×10^{-2} m/l: ——————
Aza at 8.40×10^{-4} m/l: — — — — — —
±2 sigma shown from 2 replicates.

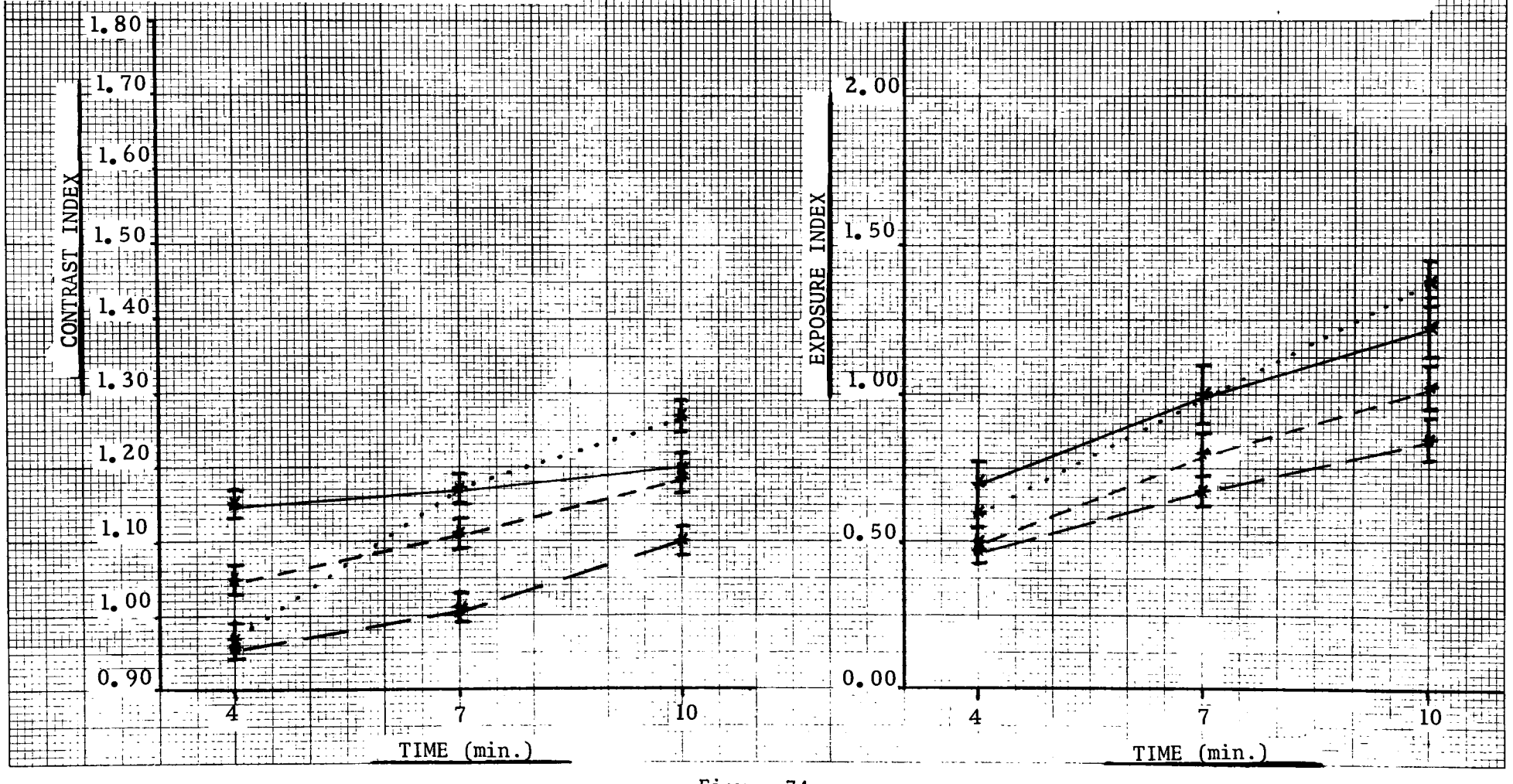


Figure 74

Density vs Log Exposure (m.c.s.)
Material: 5060
Emulsion No.: 071-5
Developer: ferro-EDTA Time: 2 min. pH: 7.0
Control: ————————————
Aza at 8.4×10^{-2} m/l: — — — — — —
Aza at 8.4×10^{-3} m/l: ————————
±2 sigma shown from 2 replicates.

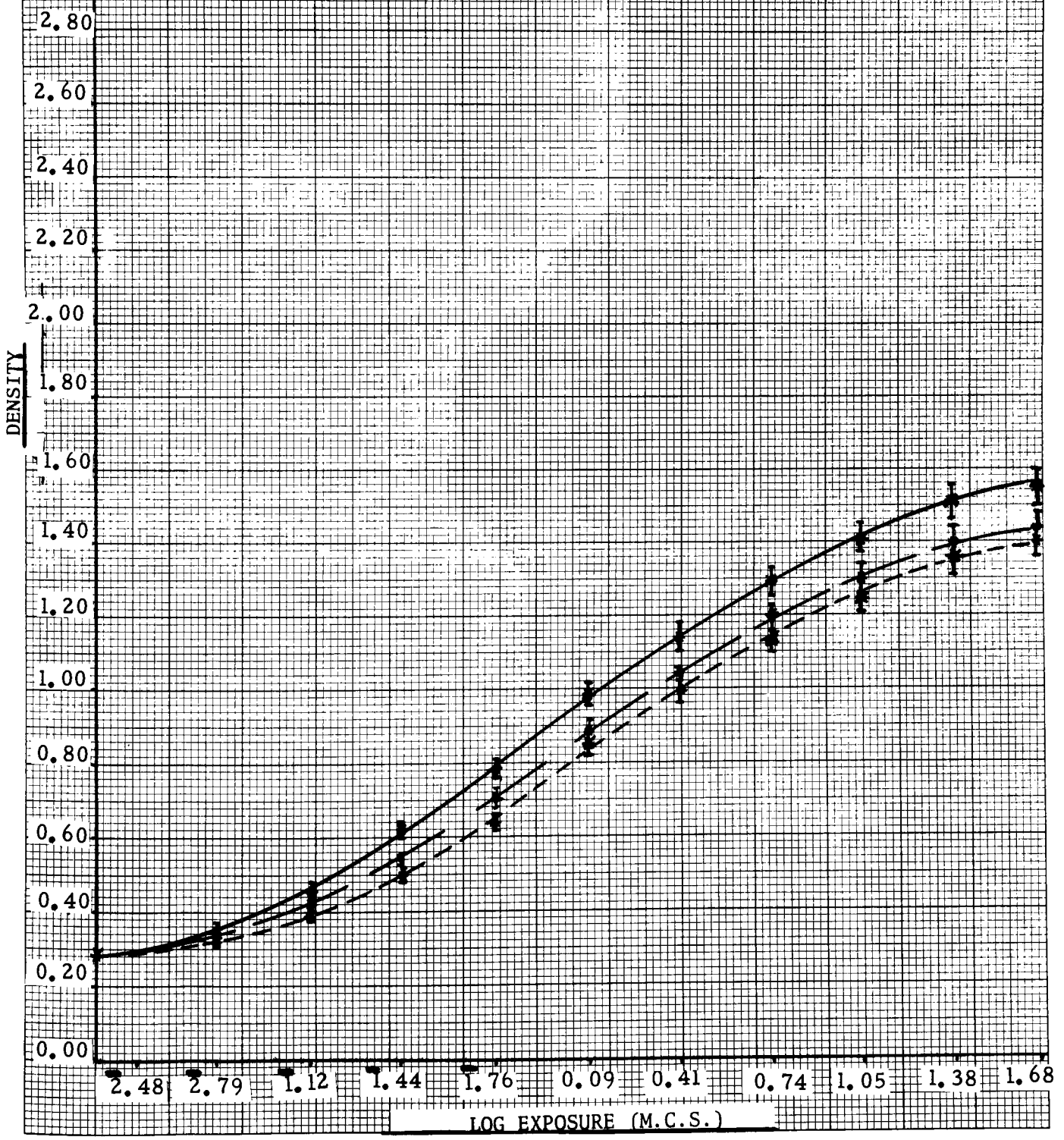


Figure 75

Density vs Log Exposure (m.c.s.)
Material: 5060
Emulsion No.: 071-5
Developer: ferro-EDTA Time: 6 min. pH: 7.0
Control: ——————————
Aza at 8.4 X 10^{-2} m/l: — — — — — —
Aza at 8.4 X 10^{-3} m/l: - - - - - - - - - -
±2 sigma shown from 2 replicates.

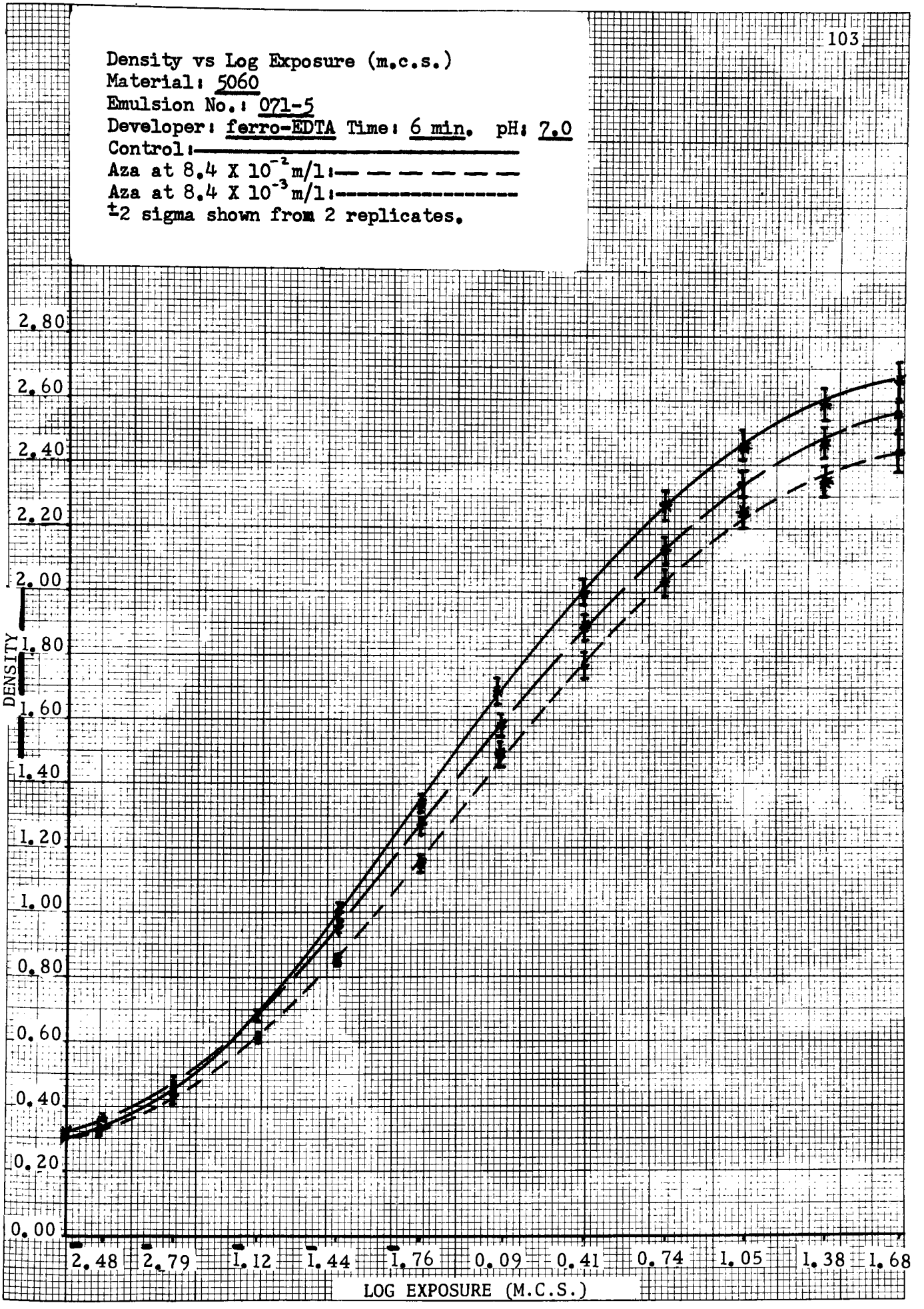


Figure 76

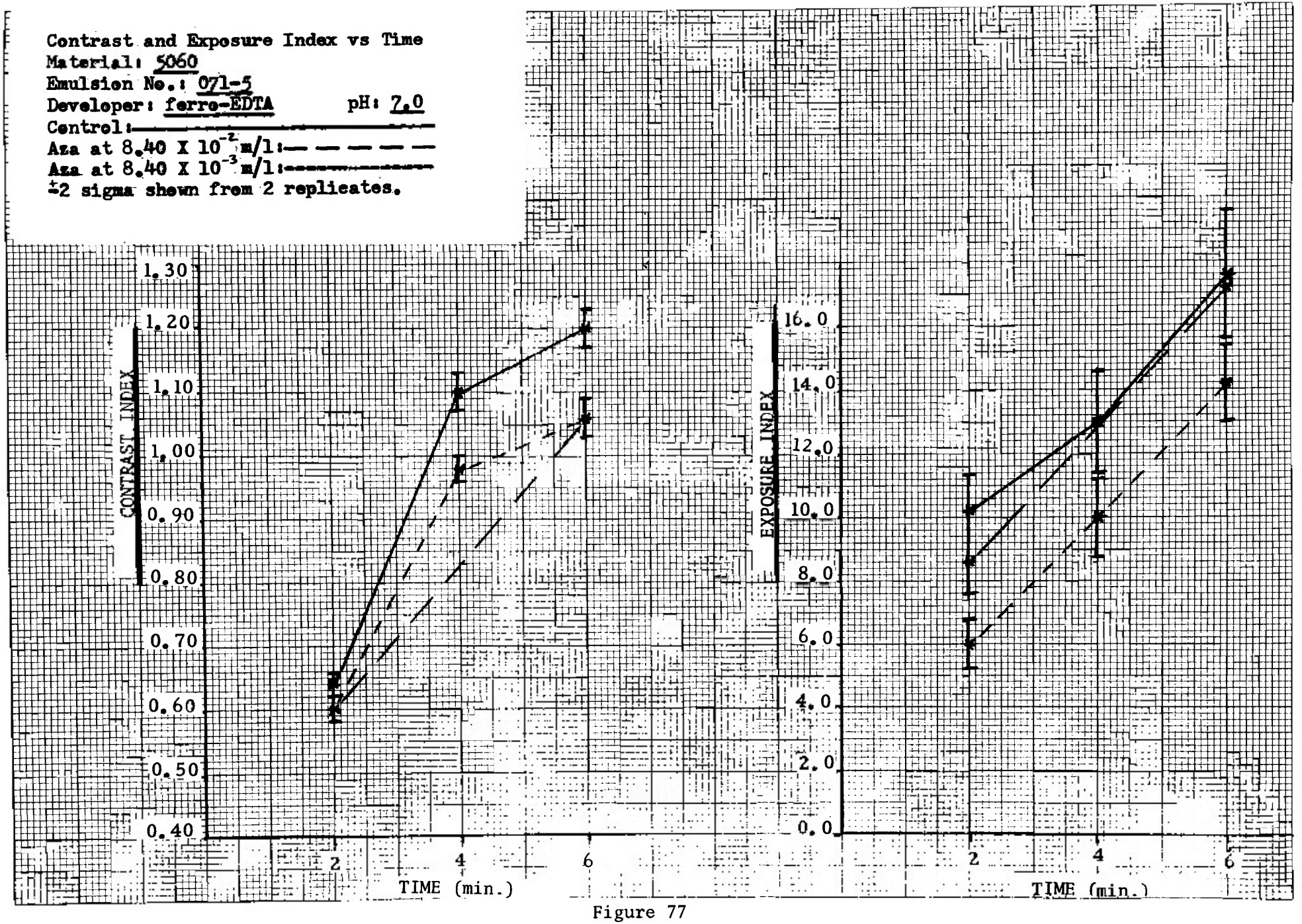

Contrast and Exposure Index vs Time
Material: 5060
Emulsion No.: 071-5
Developer: ferro-EDTA pH: 7.0
Control:
Aza at 8.40 X 10^{-2} m/l:
Aza at 8.40 X 10^{-3} m/l:
±2 sigma shown from 2 replicates.
CONTRAST INDEX
1.30
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
0.40
EXPOSURE INDEX
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
2
4
6
TIME (min.)
2
4
6
TIME (min.)

Figure 77

Increasing the concentration of Aza from 8.4×10^{-3} to 8.4×10^{-2} m/l affected the 5060 in the same manner as the 5302 film, (i.e. high levels of Aza concentration were less effective in restraint and tend to accelerate fog formation in the Fe-EDTA).

Additivity of Aza and KBr. In order to determine if Aza and KBr were more effective in restraining activity when added to Control together than individually, 8.4×10^{-3} m/l Aza and 8.4×10^{-3} m/l KBr were added to Control in one case. In the other, 8.4×10^{-3} m/l Aza and 1.68×10^{-2} m/l KBr were tested in the Fe-EDTA on 5302 film at pH 7.0 as before. Results: Figures 78 through 81 are the results of case 1, and Figures 82 through 85 represent case 2.

The results of adding both Aza and KBr to the developer indicate that together they were more effective in restraining speed than either compound acting alone. The mixture also reduced the contrast index which was higher for KBr in the absence of Aza. A slightly different system was used to calculate the contrast index for these curves. Instead of using 2.0 log E units for arc radius, an arc radius of 1.35 log E units was used to accommodate the date more accurately.

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 4 min. pH: 7.0
Control: ————————————
Aza at 8.40×10^{-3} m/l: ·····
KBr at 8.40×10^{-3} m/l: — — —
Aza plus KBr in above quantities: — —
$\pm$2 sigma shown from 2 replicates.

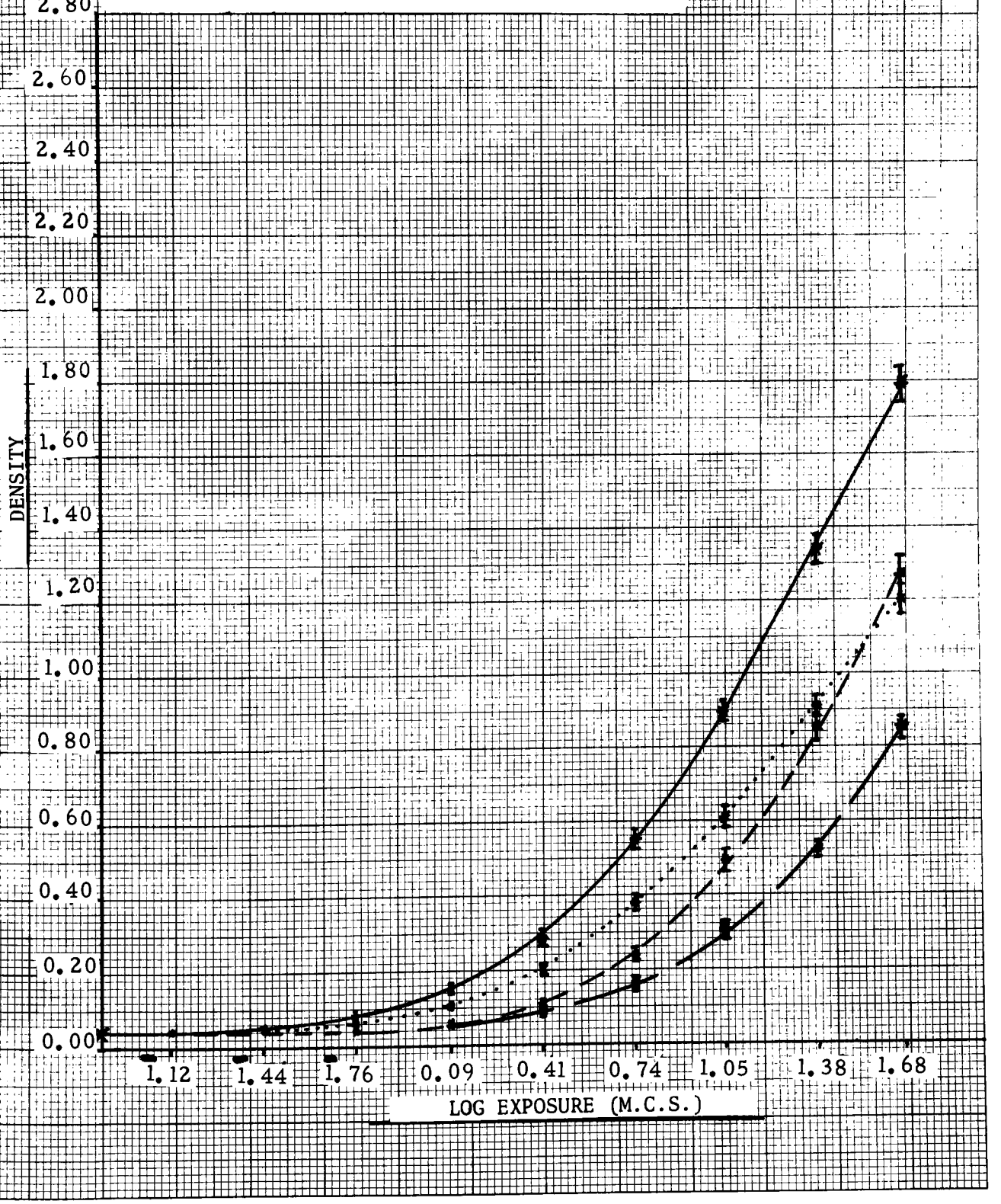


Figure 78

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 8 min. pH: 7.0
Control: ————————————
Aza at 8.40×10^{-3} m/l: ••••••••••••••••
KBr at 8.40×10^{-3} m/l: ————————————
Aza plus KBr in above quantities: — —
±2 sigma shown from 2 replicates.

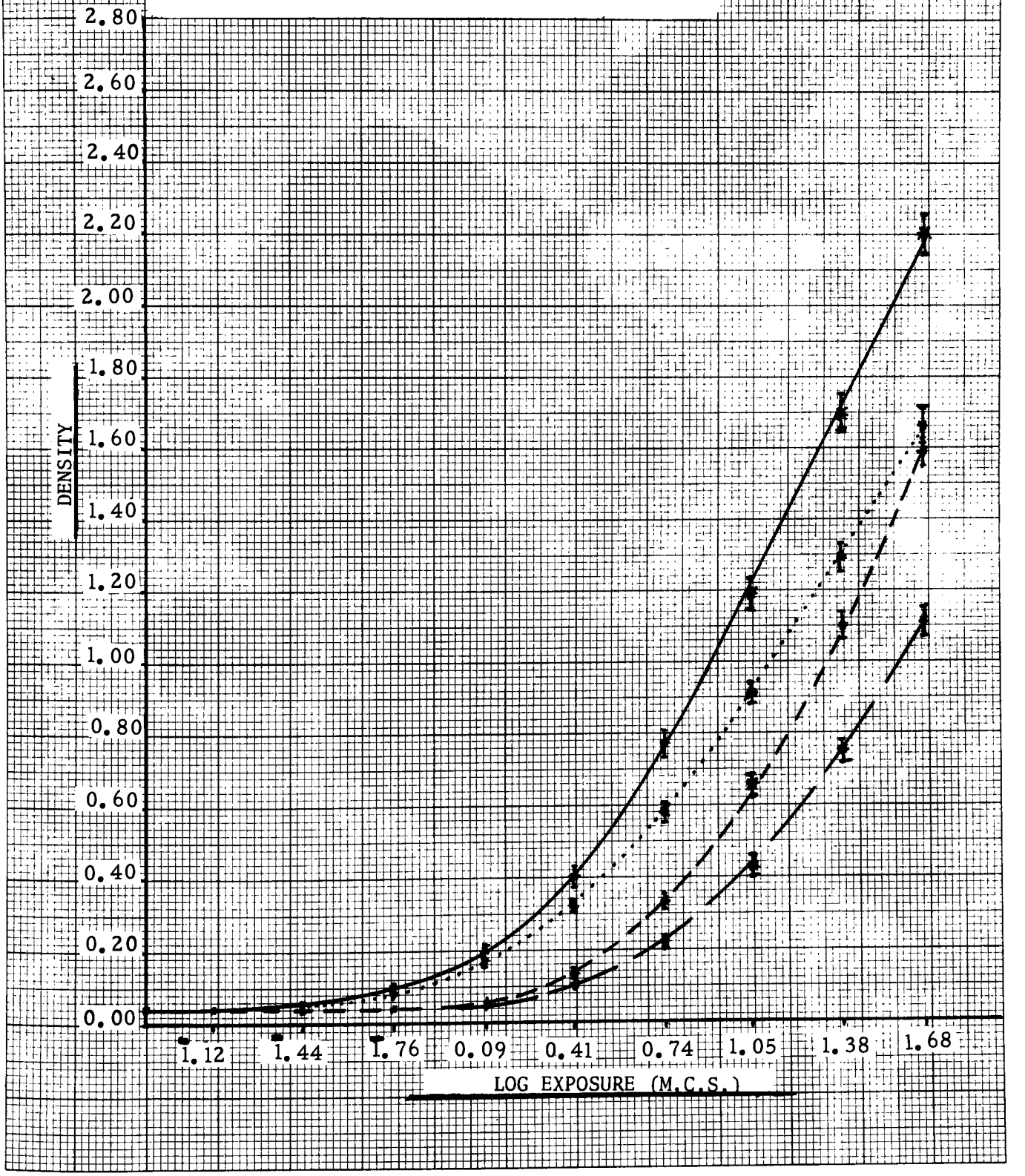


Figure 79

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 12 min. pH: 7.0
Control: ————————————
Aza at 8.40 X 10^{-3} m/l: ·····
KBr at 8.40 X 10^{-3} m/l: – – – –
Aza plus KBr in above quantities: — —
±2 sigma shown from 2 replicates.

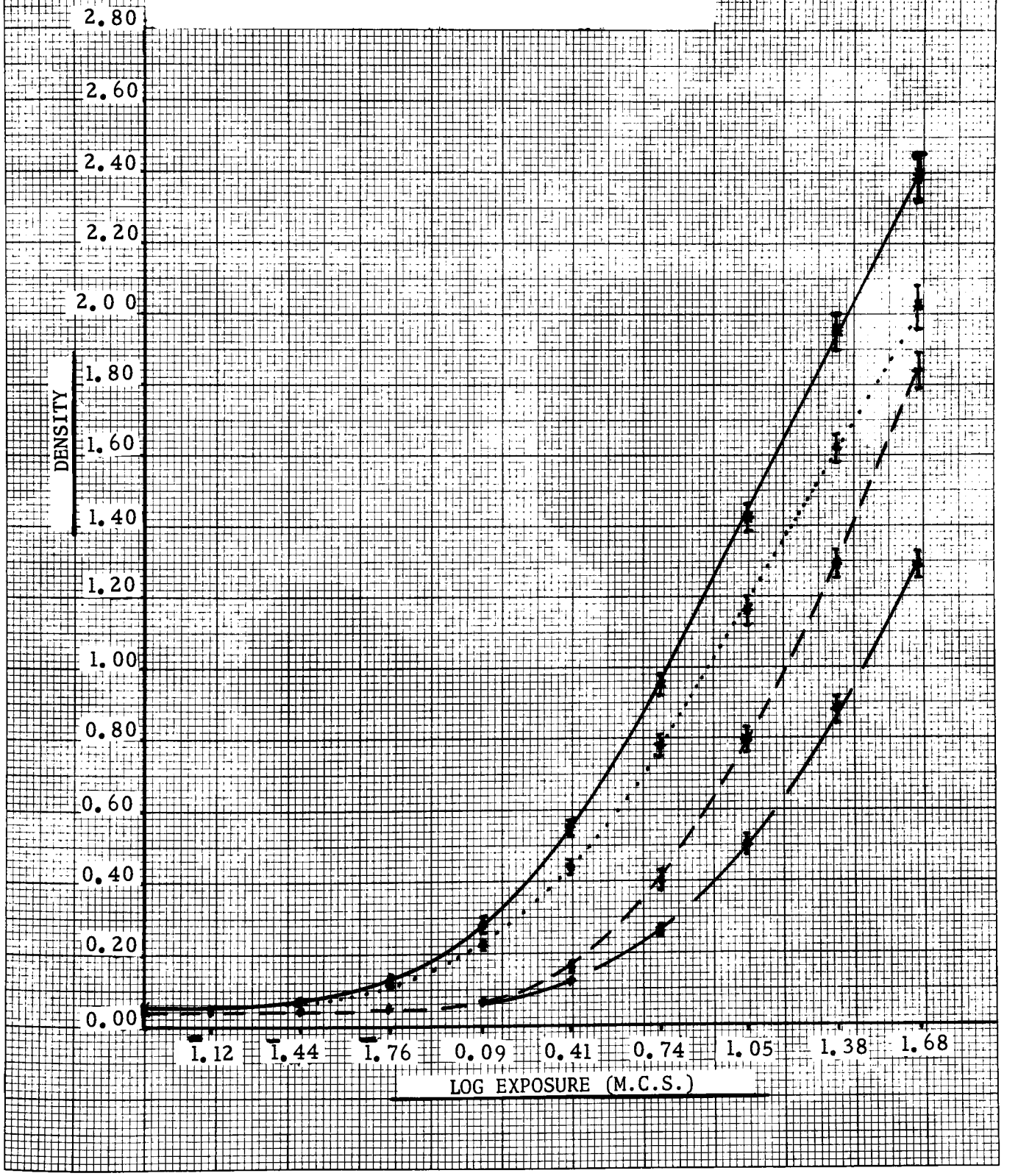


Figure 80

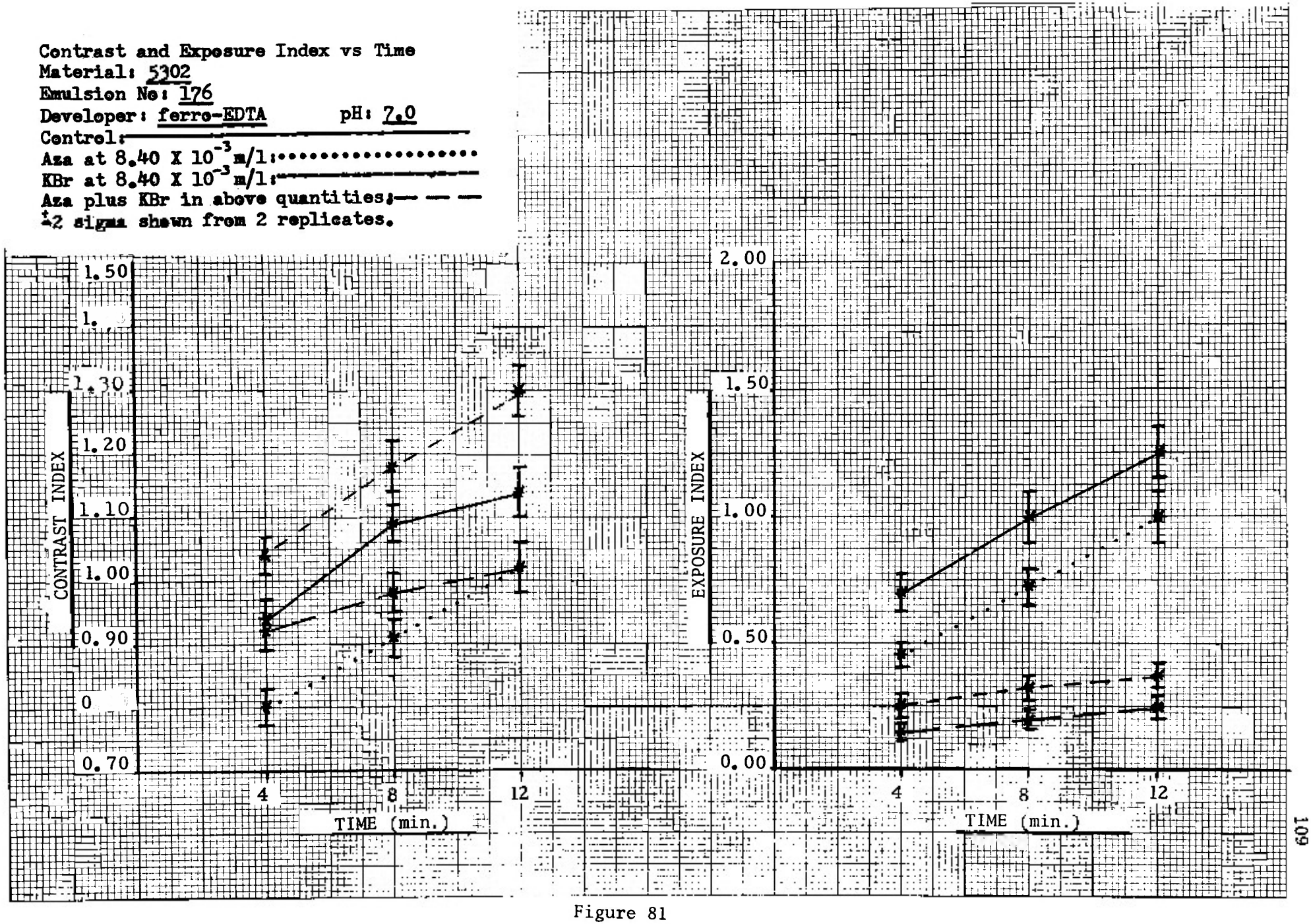

Contrast and Exposure Index vs Time
Material: 5302
Emulsion No: 176
Developer: ferro-EDTA pH: 7.0
Control:
Aza at 8.40 X 10^-3 m/l:
KBr at 8.40 X 10^-3 m/l:
Aza plus KBr in above quantities:
±2 sigma shown from 2 replicates.
CONTRAST INDEX
1.50
1.30
1.20
1.10
1.00
0.90
0.70
4
8
12
TIME (min.)
EXPOSURE INDEX
2.00
1.50
1.00
0.50
0.00
4
8
12
TIME (min.)

Figure 81

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 4 min. pH: 7.0
Control: ————————————
Aza at 8.40×10^{-3} m/l: ·····
KBr at 1.68×10^{-2} m/l: – – – –
Aza plus KBr in above quantities: — —
± 2 sigma shown from 2 replicates.

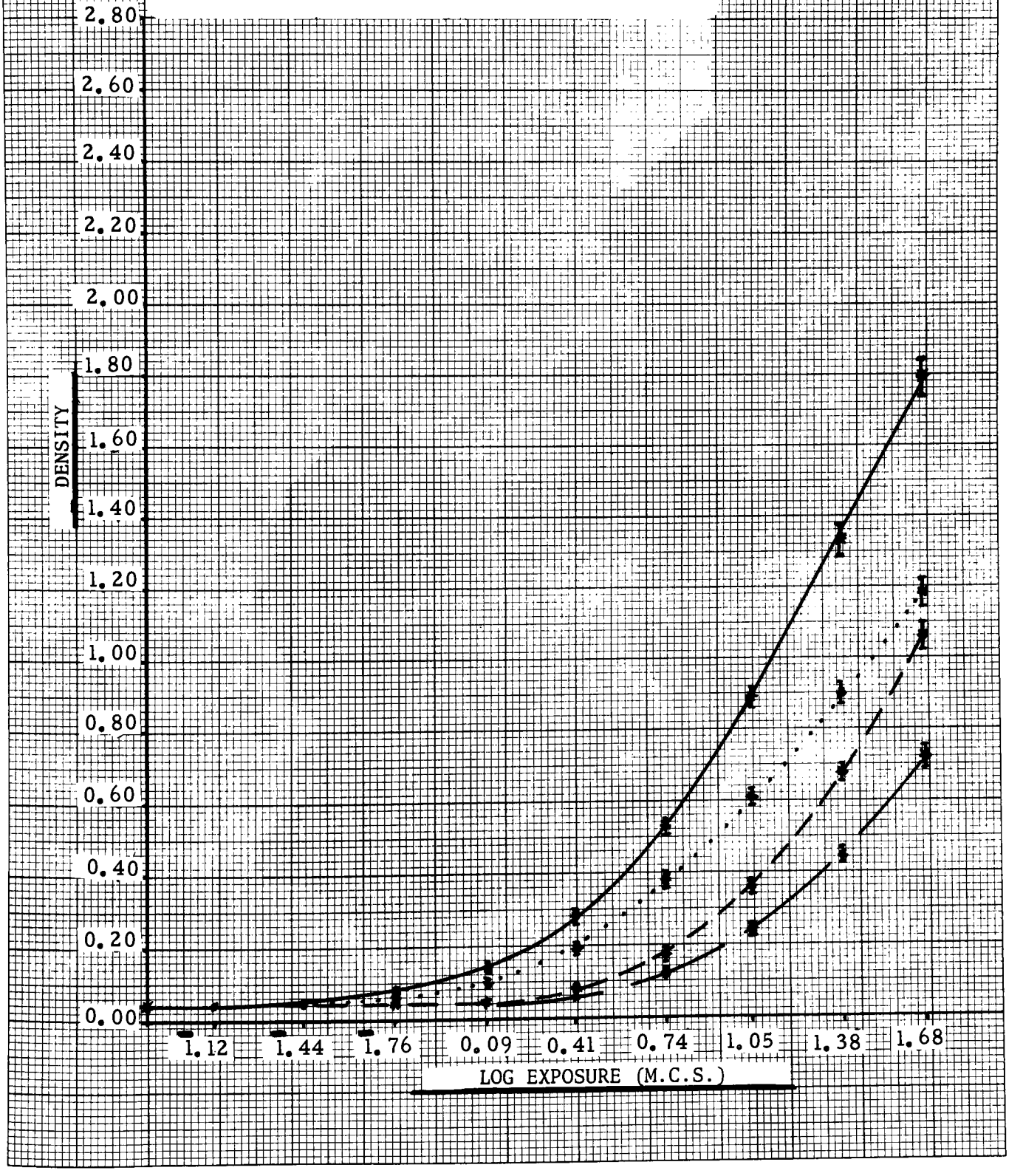


Figure 82

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 8 min. pH: 7.0
Control: ————————————
Aza at 8.40×10^{-3} m/l: ....
KBr at 1.68×10^{-2} m/l: – – – – – – – –
Aza plus KBr in above quantities: — —
±2 sigma shown from 2 replicates.

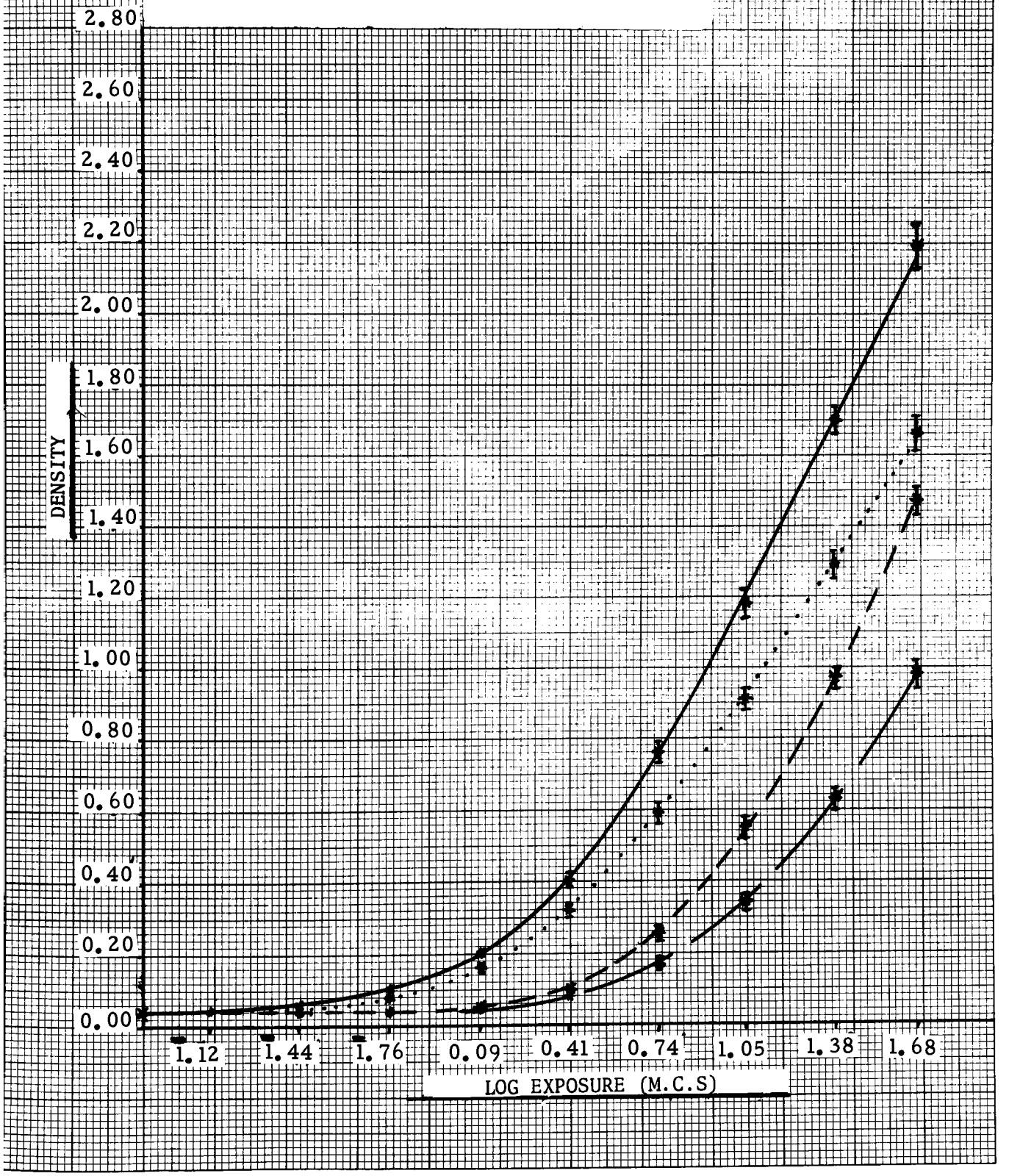


Figure 83

Density vs Log Exposure (m.c.s.)
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA Time: 12 min. pH: 7.0
Control: ————————————
Aza at 8.40×10^{-3} m/l: ••••••••••••••
KBr at 1.68×10^{-2} m/l: — — — — — —
Aza plus KBr in above quantities: — —
± 2 sigma shown from 2 replicates.

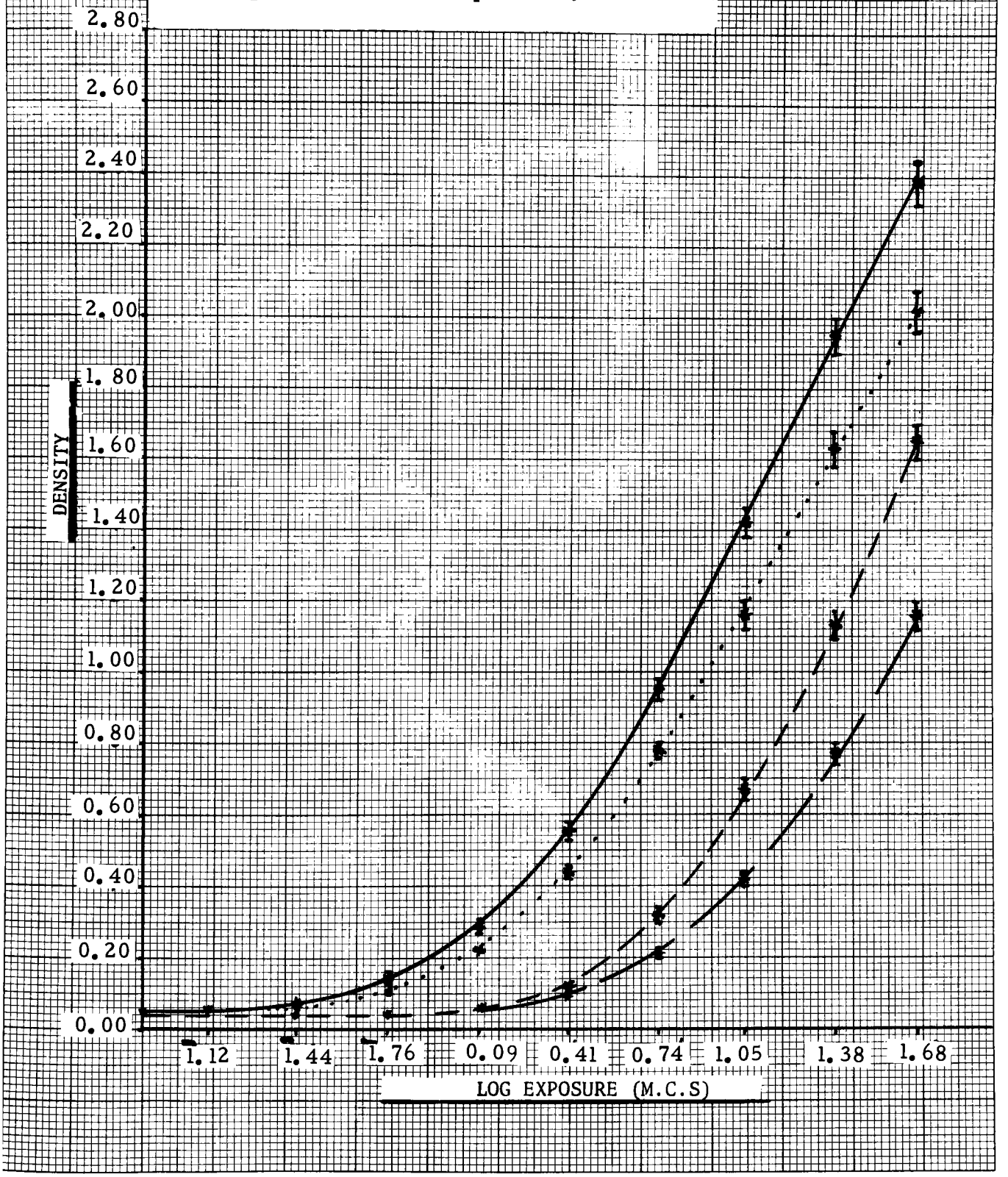


Figure 84

Contrast and Exposure Index vs Time
Material: 5302
Emulsion No.: 176
Developer: ferro-EDTA pH: 7.0
Control: ———————
Aza at 8.40×10^{-3} m/l: ·····
KBr at 1.68×10^{-2} m/l: — — —
Aza plus KBr in above quantities: — — —
±2 sigma shown from 2 replicates.

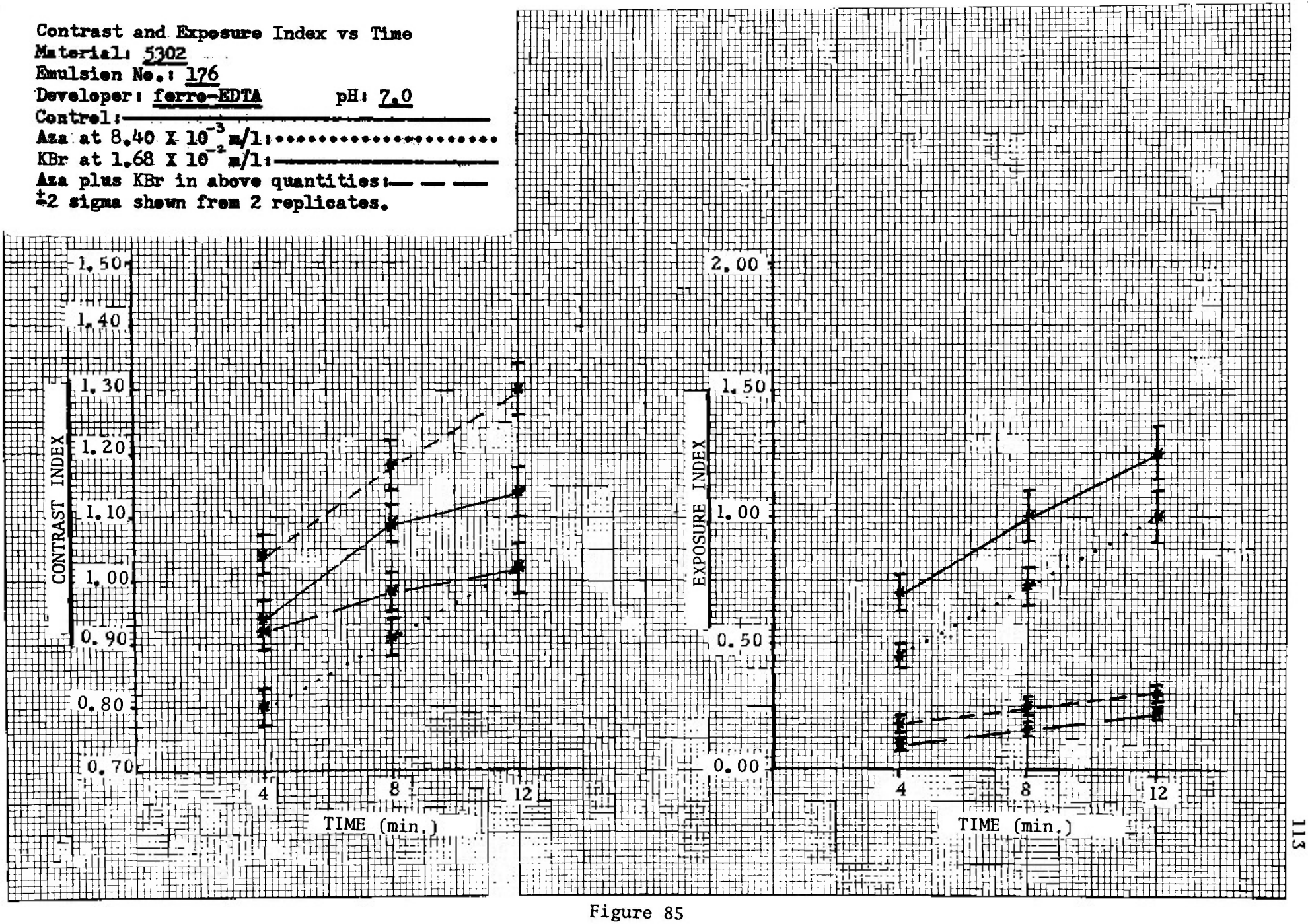


Figure 85

Discussion

The sensitometric evaluation of the effects of Aza and KBr in development clearly indicate that Aza was both an antifoggant and development restrainer at emulsion pH (6 to 7). Aza differed slightly from KBr in that it selectively repressed contrast more than the bromide.

Birr[19] has postulated two types of stabilizing mechanisms. In the first, the stabilizer is adsorbed and restrains the catalytic action of the nuclei by selective adsorption. The heterocyclic mercaptans, which give marked emulsion stabilizing action in amounts, (5 to 20 mg/mol AgX), that can cover only 1 to 2-percent of the silver halide surface and which are strongly antifoggant in development at 10^{-5} mol/l, are examples of this type mechanism. In the second case, the stabilizer is not adsorbed and has no influence on development. Aza is an example of the second case because of its weak adsorption and its desorption from development centers at the high pH values commonly encountered in standard MQ developing solutions. Birr[28] has shown that Aza behaves similarly to the heterocyclic mercaptans if the alkyl radical in the six position contains a carbon chain length of four or more. According to Birr[28], the favorable stabilizing effect of Aza is a result of it being held at a higher level in the gelatin matrix adsorbed to the silver halide grains, and to it acting primarily by inducing formation of sulfide in this layer away from actual contact with the silver halide crystals.

The results of this work do not support the idea of two separately distinct mechanisms of emulsion stabilization, because Aza was found to be antifoggant in development at the pH of photographic emulsions which is near 6 or 7. This work has also provided evidence that Aza is desorbed at the high pH values of the common developing agents as shown by the decrease in restraining ability of Aza at high pH. Previous investigations[19,20,27] have shown that Aza is inactive in common MQ developers with pH values near 10. This work has extended those investigations, and the data show that in the same developer the activity of Aza in restraining development varied with pH. Aza was even noted to accelerate fog formation at high pH.

Aza restrained the rate of development of a simple silver halide emulsion, (5302 film), in Amidol at pH 6.0. Faerman[8] has also shown that Aza restrained the rate of reduction of exposed silver bromide sols, (in the presence of gelatin), when the sols were reduced by Amidol at low pH, (i.e. 5.0).

At pH 7.0 an increase in the concentration of Aza beyond 3.78×10^{-2} m/l had only a small effect on the rate of reduction of 5302 film by Amidol. In Faerman's[10] investigation on the effect of Aza on the rate of reduction of silver bromide sols by Amidol, the extent of restraint by Aza increased as the concentration of Aza was increased from 5×10^{-4} m/l to 2×10^{-3} m/l where the restraining activity became constant. Both of these results are evidence of a Langmuir-type adsorption isotherm of Aza on silver halide. The acceleration of development and fog formation by Fe-EDTA on 5302 and 5060 films in the presence of high concentrations of Aza at pH 7.0 was apparently due to some new unexplained factor. Independent evidence would be necessary to identify specifically what occurred in the Fe-EDTA

developing solution, in the presence of Aza at concentrations above 3.78×10^{-2} m/l, that apparently rendered the developer a stronger reducing agent. This effect was not observed on 5302 film processed in Amidol at the same pH.

The fact that Aza showed a selective repression in that it decreased contrast more than KBr indicates that Aza and KBr restrained development by acting according to two different mechanisms. The evidence that Aza and KBr showed additivity in restraint of 5302 film processed in Fe-EDTA at pH 7.0 supports the idea of two different mechansims, although not conclusively. Increasing the concentration of KBr from 1 to 2 grams/liter had only a small effect on increased restraint of the 5302 film. Therefore, it can be assumed that the silver halide was near saturation with Br^- ions at 1 gram/liter, (or 8.4×10^{-3} m/l). The developer with Aza had no Br^-, and on development of the latent image Br^- was released. Since Aza and KBr were additive in their restraint of development, it can be assumed that the Br^- released during development added to the restraining ability of Aza, thereby causing Aza to show greater restraint of the higher densities.

The results of this work along with the evidence previously cited do not support the two mechanism of emulsion stabilization concept of Birr[19]. Birr[16] found, that at concentrations of Aza of the order used in practice, not more than 5 to 10 percent is adsorbed in the liquid emulsion. However, since it is used at 1 to 2 grams/mol AgX, while the mercaptans are used at 5 to 20 mg/mol AgX, the amounts adsorbed are similar. The evidence further indicates that Aza is adsorbed on the silver halide grains at emulsion pH when present in concentrations normally used. Antifoggant and restraining action by Aza in the developer at emulsion pH may depend on the covering of active areas in unexposed and exposed grains by Aza. Because Aza

is adsorbed to the same extent as the mercaptans, when present in amounts normally used, it is unnecessary to assume two distinctly different mechanisms of emulsion stabilization. The fact that Aza causes no desensitization or restraining action during normal development is explained by its desorption from development centers at the high pH of the commonly used MQ developers. The reason for the superiority of Aza over the mercaptans as an emulsion stabilizer remains unexplained.

SECTION 2

This section describes the displacement of a constant concentration of 1, 1'-diethyl-2, 2'-cyanine iodide dye by three different concentrations of Aza in a pure silver bromide emulsion before and after drying.

Experimental Procedure. The procedure for the preparation of the pure silver bromide emulsion is located in Appendix B.

The amount of dye used for each determination was 0.15 gram dye/mol AgBr. 100 mg of the dye (EASTMAN order number 7851; lot number 691-1) were dissolved in methyl alcohol in a 100 ml volumetric flask. The silver bromide emulsion contained about 0.10 mol AgBr/430 grams of the emulsion. Small portions (about 40 grams) of the gelled emulsion were weighed and the necessary amount of dye solution was calculated for the exact weight. Aza was added to the emulsion at 0.2, 2.0, and 3.0 g/mol AgBr.

The spectral absorption of the dye in dried gelatin was measured. A detailed description of the procedure is in Appendix C. It was found that there were two absorption bands, one with maximum at 495 nm and another near 530 nm. These peaks served as references in determining the effects of Aza in deaggregating or displacing the dye in the silver bromide emulsion. Aza had no effect on the two peaks of the dye in the dried gelatin.

The weighed silver bromide emulsion was placed in a 1 liter stainless steel beaker which was covered with aluminum foil and placed in a water bath maintained at 55C. When the emulsion was completely melted, the dye was added and allowed to digest 15 minutes at 55C. When Aza was added, it was added to the melted emulsion first and given the 15 minute digestion at 55C, after which the dye was added and allowed to digest 15 minutes at 55C. The two resulting emulsions were hand coated on 5 inch by 7 inch clear cellulose acetate sheets with the 0.009 inch clearance coating knife after the addition of 3 or 4 drops saponin solution for uniformity. The sheets were held tightly against a flat temperature-controlled aluminum plate by vacuum. The plate was kept warm enough during coating so that the emulsion would flow readily, then chilled to set it. The acetate sheets were then cut into 8 pieces. These small wet pieces were placed emulsion side up on sheets of aluminum foil that were placed on top of cracked ice in a styrofoam ice chest. This was to minimize moisture loss and to maintain the samples as firm as possible prior to insertion into the Beckman DK-2A Spectrophotometer described in the Introduction. It was found that if this were not done, the samples began to melt long before the spectral scan was completed causing non-uniformity from a varying coating thickness.

Even though much care was taken to coat uniformly, there still appeared differences in coating thickness within each sheet as evidenced by the initial reflectance values at 730 nm of the wet samples. The thicker the coating the higher the reflectance. 730 nm is referred to as the initial value because the instrument began at 730 nm and scanned down to 380 nm. The initial reflectance values at 730 nm

varied from 55% to 75%, but most of the samples had values between 64% and 67%. Therefore, only samples in the range 64-67% were selected as being in tolerance and all others were rejected. This was an arbitrary selection, and one possible way of reducing the effect due to varying coating thicknesses.

All samples were scanned as soon as possible after coating and icing. It was found that as soon as 45 minutes after coating, the initial reflectance values were out of tolerance due to water loss and reduced reflectance, even though the samples remained on ice and were covered. The reflectance spectrum was run first with the black background of the compartment as the backing, (i.e. the sample holder was removed), so that the sample holder would not contribute to the total reflectance. After the reflectance spectral scan of a particular sample was made, that sample was returned immediately to the ice chest, and the instrument set up for the transmission mode as quickly as possible. The sample was then removed from the ice chest, placed in the sample port, and spectrally scanned for transmission. This procedure proved to be repeatable to within ±1% absorbance, and it was only required for the wet analysis. After the wet samples were scanned, they were allowed to dry 24 hours at room temperature.

The wet samples showed no evidence of print-out from being exposed by the spectrophotometer. This was verified by running the scan of the sample twice and observing no appreciable spectral change.

As mentioned previously[31], there is a competitive adsorption interaction between Aza and certain carbocyanine dyes on silver halide for which there is an equilibrium for any particular given set of conditions. If Aza becomes effectively more concentrated in the dried emulsion and more is adsorbed, then the equilibrium between Aza and dye adsorbed on silver halide would shift toward more Aza adsorbed in the dry emulsion. If this were the case, there would be a greater decrease in the J-band of the dye in the dry emulsion than in the wet with Aza present.

In order to determine if this shift in equilibrium actually occurred on drying, Aza was added to the emulsion at 0.2, 2.0, and 3.0 g/mol AgBr with 0.15 g dye/mol AgBr present in all three cases. The samples were spectrally scanned as previously described.

Results. The actual spectral scans are located in Appendix D. Figure 86 shows how 2.0g Aza/mol AgBr affected the dye in the wet emulsion. Control represents dye in the absence of Aza. A wavelength by wavelength calculation of absorbance was made for the graph from the reflectance and transmittance scans. ±2 Sigma limits are indicated on peak absorbance values. The limits were determined from 6 Control replicates and 5 Aza replicates.

From the graph it is obvious that Aza not only decreased the J-band strength of the dye at 575 nm but also caused the appearance of two bands, previously identified as unaggreagated dye in gelatin, with maxima at 495 nm and 530 nm. It is, therefore, quite reasonable to

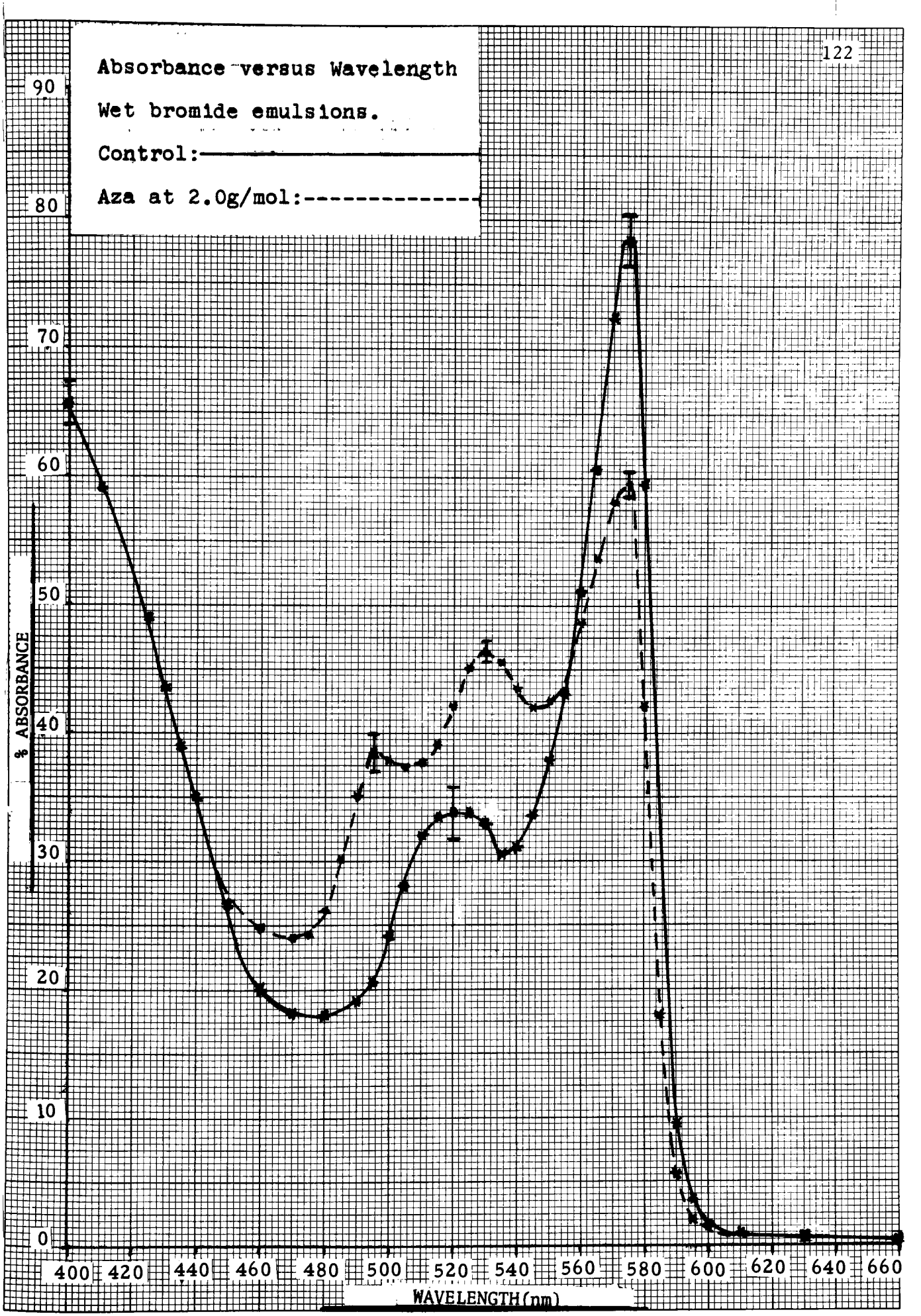

Absorbance versus Wavelength
Wet bromide emulsions.
Control:
Aza at 2.0g/mol:
90
80
70
60
50
40
30
20
10
0
% ABSORBANCE
400
420
440
460
480
500
520
540
560
580
600
620
640
660
WAVELENGTH(nm)

Figure 86

assume that Aza not only deaggregated the dye, but also displaced it from the surface of the silver bromide grains. Along with the appearance of the bands at 495 nm and 530 nm in the presence of Aza was the apparent disappearance of the 520 nm absorbance peak in the Control. If the 520 nm band in the presence of Aza still existed, it could no longer be identified. The 520 nm band is not an M-band because it is too short. However, it could be an H-band.

A slight increase in apparent absorbance was observed on the dried samples. The probable cause of this increase over that of the wet samples was that on drying, the samples curled inward toward the emulsion side. Since the sample holder had been removed, the samples curled inward toward the integrating sphere even though taped to the sides of the reflectance port of the sphere. The rays incident on a flat sample, flush against the sphere, are at a five degree angle to the surface, and the specular component of the reflectance of the sample is incident at a point half way between the entrance and exit ports of the sphere. However, the dried samples were curled and acted as parabolic mirrors, with respect to the specular component. As a result, part of the specular component was lost through the entrance and or exit ports of the integrating sphere. This loss in reflectance naturally increased the apparent absorbance values for all dried samples. That it was due to reflectance is evidenced by a proportionately greater decrease in reflectance than increase in transmittance on drying. The increase in apparent absorbance on drying was from 3 to 7% and relatively independent of wavelength. This effect did not inhibit the analysis, however. For future experiments of this nature, a flat backing covered with black velvet,

(for low reflectance), could be placed flush against the dried samples with the sample holder in place to eliminate the curl. The wet samples did fit flush against the sphere, and , consequently, the problem never arose. The sample holder should not be used to press the wet samples against the sphere. Any pressure of this nature would cause the pliable emulsion to change shape, and this would result in coating thickness errors. The same black velvet backing used on the dry samples should be taped to the back of the wet samples, but without the sample holder in place applying pressure. This procedure would provide equivalent backings for both conditions.

The ratio of the J-band absorption at 575 nm to a reference at 400 nm was used as the response variable for the analysis. Since practically all absorption at 575 nm is due to the aggregated dye and practically all absorption at 400 nm is due to silver bromide, taking the ratio of these two absorbance values tends to cancel coating thickness errors.

Table 1 gives the absorbance values of the wavelengths of interest for each of the conditions tested. ±1 Sigma limit is given from the number of replicates indicated. Only the maximum values of the absorbance peaks have been recorded.

The table emphasizes the fact that the higher values of the dry emulsions are relatively independent of wavelength. This has already been explained in detail in Section 2 .

Condition	Replicates	Wavelength nm 575	530	520	495	400
No Aza dry	6	81.3 ± 0.9	-	37.1 ± 1.6	-	70.4 ± 0.9
No Aza wet	6	78.5 ± 0.8	-	34.1 ± 1.2	-	65.7 ± 0.8
0.2g Aza dry	6	72.6 ± 1.0	-	42.0 ± 1.0	-	71.0 ± 1.1
0.2g Aza wet	6	65.1 ± 0.5	-	37.5 ± 1.0	-	65.0 ± 0.7
2.0g Aza dry	5	64.2 ± 0.9	50.2 ± 1.0	-	41.9 ± 0.9	70.2 ± 0.7
2.0g Aza wet	5	59.6 ± 0.4	46.3 ± 0.4	-	38.0 ± 0.8	64.7 ± 0.3
3.0g Aza dry	2	61.2 ± 1.2	45.5 ± 1.0	-	36.9 ± 1.6	67.5 ± 0.7
3.0g Aza wet	2	57.1 ± 0.5	42.2 ± 0.5	-	33.7 ± 0.7	62.0 ± 0.5

TABLE 1

PERCENT ABSORPTION OF PEAKS FOR GIVEN CONDITIONS

Figure 87 shows the ratios plotted against the three concentrations of Aza.

The graph shows that the highest ratio was, of course, the dye in the absence of Aza. On the addition of 0.2 and 2.0g Aza/mol AgBr, significant decreases in the ratios were observed. There was no further significant change noted in the equilibrium between AgBr, Aza, and dye in going from 2 to 3g Aza/mol AgBr. The ±2 sigma limits were obtained from 6 replicates of dye in absence of Aza, 6 replicates of 0.2g Aza/mol, 5 replicates of 2.0g Aza/mol, and 2 replicates of 3.0g Aza/mol. The sigma limits of the latter are larger due to the small sample size. For each of the four cases depicted on the graph , there was no significant difference in the ratios of the wet and dry samples.

There was the possibility that Aza influenced the solubility of the dye in the wet emulsion. Any increase in the solubility of the dye in the wet emulsion with Aza present and subsequent decrease in dye solubility in the same emulsion after drying would influence the results by decreasing the J- band strength of the dye more in the wet than in the dry emulsion with Aza present. This effect would be in opposition to the expected results. Therefore, a test was made utilizing the principle of partition coefficients. The test is described in detail in Appendix E.

The results of the test indicate that concentrations of Aza up to 8.4×10^{-3} m/l did not materially influence the solubility of the dye in the aqueous phase. This concentration of Aza was not exceeded in the dye displacement study.

Ratio of J-band to Reference at 400nm versus Grams Aza/mol Silver Bromide.

±2 sigma limits indicated.

No significant difference in ratio noted on drying the emulsion.

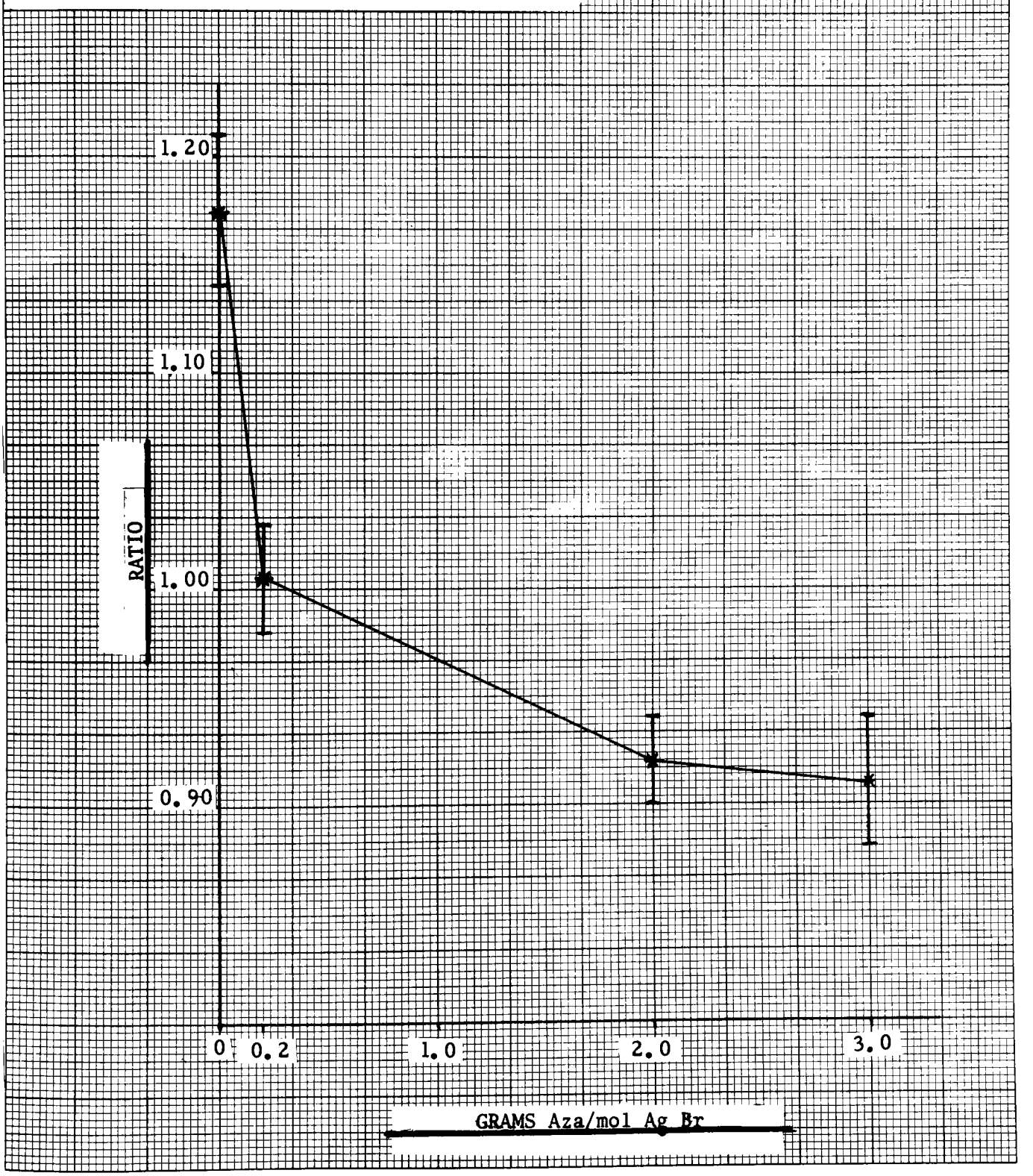


Figure 87

Discussion. There has been no explanation given in the literature as to what the concentration of Aza or any compound in a dried emulsion coating actually means as related to adsorption equilibrium. Because adsorption of Aza on AgBr is governed by a Langmuir-type isotherm[34] and because Aza did not increase the solubility of the dye in the aqueous phase, the results of this work indicate that on drying the emulsion there was no further increase in the adsorption of Aza on AgBr as a result of any effective increase in concentration, as evidenced by no significant increase in dye displacement on drying.

Aza at 2.0g/mol was tested first, and there was the possibility that the surface of grains in the wet emulsion was saturated with Aza at that level. If this were the case, there would be no change in the amount of dye displaced on drying the coating. There could be a change at a lower level of Aza, because the surface would not be saturated in the wet coating. Then if the surface were not saturated, any increase in the amounts of Aza adsorbed and dye displaced as a result of an increase in the concentration of Aza on drying could be detected. Therefore, a lower concentration of Aza (0.2g/mol AgBr) was tested. The ratio of the J-band absorbance of the dye to the reference absorbance of AgBr at 400 nm was higher at the lower level of Aza in both the wet and dry coatings indicating that the grain surface was not saturated by Aza at 0.2g/mol. To test the possibility of saturation by Aza at 2.0g/mol a higher concentration of Aza was used, (i.e. 3.0g/mol). Since no further significant decrease in the ratio was noted on the addition of 3.0g/mol, it can be assumed that the grain surface was probably saturated with Aza at 2.0g/mol.

CONCLUSIONS

At the pH of photographic emulsions, (near 7.0), and in concentrations of Aza normally used in the emulsions, (1 to 2 grams/mol AgX), Aza, like KBr, was both a restrainer and an antifoggant during the development of 5302 film by Amidol at pH 6, 7, and 8 and the ferrous ethylenediaminetetraacetate (EDTA) complex ion at pH 4.5 and 7. Type 5060 film processed in Fe-EDTA at pH 4.5 and 7 gave similar results. The restraint by Aza on development decreased at pH values above 8.5. Aza increased fog in 5302 film processed in Fe-EDTA at pH 8.5 and 10.0. Aza did not increase fog on 5060 film under the same conditions, however, it did do so when 5060 film was processed in an MQ developer at pH 10.3.

Increasing the concentration of Aza from 8.4×10^{-3} to 8.4×10^{-2} m/l decreased the rate of development, but only to a relatively small degree, when 5302 film was processed in Amidol at pH 7.0. However, Aza in concentrations of 3.78×10^{-2} and 8.4×10^{-2} m/l in Fe-EDTA increased fog and development rate of both 5302 and 5060 films at pH 7.0.

Aza at 8.4×10^{-3} m/l in the presence of KBr at 8.4×10^{-3} and 1.68×10^{-2} m/l in Fe-EDTA decreased the rate of development of 5302 film at pH 7.0 to a greater extent that either used alone.

The above evidence does not support Birr's[19] concept of two distinctly different mechanisms of emulsion stabilization.

Section 2 of this work provides results that indicate Aza not only decreased the J-band absorption at 575 nm of 1, 1'-diethyl-2, 2'-cyanine iodide dye in a silver bromide emulsion but also caused the appearance of two bands, identified as unaggregated dye in gelatin, one with maximum at 495 nm and the other near 530 nm. This is evidence that Aza not only deaggregated the dye but also displaced it from the silver bromide. This displacement of dye by Aza did not increase on drying the emulsion at high concentrations of Aza, (2 to 3 grams/mol AgBr), where the grain surface was saturated with Aza, as well as at a low concentration of Aza, (0.2 grams/mol AgBr), where the grain surface was not saturated with Aza. This evidence indicates that the adsorption equilibrium between Aza and dye on silver bromide did not significantly change on drying the emulsion in spite of the change in the concentration of Aza from the wet to dry emulsion.

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APPENDICES

APPENDIX A

PURITY DETERMINATION OF AZA COMPOUNDS

One of the best methods of verifying the purity of organic compounds is by mixed melting point determinations. This procedure involves mixing a sample of unknown purity with a pure sample of the same compound. If there is no significant depression in the melting point of the pure sample, then it is relatively certain that the sample under test contains no appreciable amounts of impurities.

Pure Aza melts at 278C with decomposition.[24] The Kodak sample was assumed to be pure and used as a reference to test the Aldrich Aza. Since the Kodak Aza was present as the sodium salt, it was necessary to obtain it as the free phenol in order to determine its melting point. The sodium salt was dissolved in distilled water in a test tube, and the solution was placed in an ice bath. Dilute HCL was added slowly until the free phenol began to precipitate. The free phenol was then filtered from the solution and washed four times with cold distilled water to remove the HCL. The crystals were then dried under vacuum for five hours. The Fisher Johns melting point apparatus was used for the analysis. Since the absolute value of the melting point was not required, it was not necessary to calibrate the apparatus. The KODAK Aza melted at 282-285C with decomposition. The Aldrich Aza melted at 283-286C with decomposition. Equal amounts of the two compounds were mixed well with a mortar and pestle. The melting point of this mixture was 283-285C. This was a very good indication that both compounds were of the same purity.

A further verification of purity was made by potentiometric titration of both Aza compounds with silver nitrate. Pure Aza forms an insoluble salt with silver almost as insoluble as AgCl. Potentiometric

titrations are used to determine the solubility products of insoluble salts. As silver nitrate is added to Aza the salt begins to form by $[Aza]^-$ removing silver ions from the solution as evidenced by an increase in potential between the reference and silver electrodes. The equilibrium concentration of silver ions determines the solubility product of the salt. Pure Aza should adhere to this pattern of behavior by giving a smooth titration curve. Any impurities could be detected by irregularities in curve shape or position.

Solutions of both compounds were prepared with Aza at 0.01 m/l in a 0.01 M sodium acetate buffer. The pH was then adjusted to 7.0 with acetic acid. The pH was continuously monitored throughout the titration and maintained at 7.0 with acetic acid. Both solutions were titrated separately with 140 ml of a 0.01 molar solution of silver nitrate.

Figure 88 shows the results for the Aldrich Aza and Figure 89 for the Kodak Aza.

The smooth curve shape characteristic of both compounds, the agreement of the titrations within 2% in volume of $AgNO_3$, and the agreement of both curves within error of observation in midpoint voltage are indications that both compounds were of the same purity.

The solubility product of the silver salt of Aza from the titrations at 23.5C was determined. Since the exact potential of the calomel reference electrode, which had a nitrate bridge, was not known, a solution with a pAg of 9.0 was prepared by adding 0.05g KBr to 1 liter of a saturated solution of AgBr in water. The reference electrode was then used in conjunction with the silver electrode in the solution to measure the cell potential. The potential of the reference electrode was then calculated from the following equation:[38]

100 ml Aldrich Aza (0.01M) Titrated with

132 ml (0.01M) Silver Nitrate.

Temperature: 23.5C

pH: 7.0

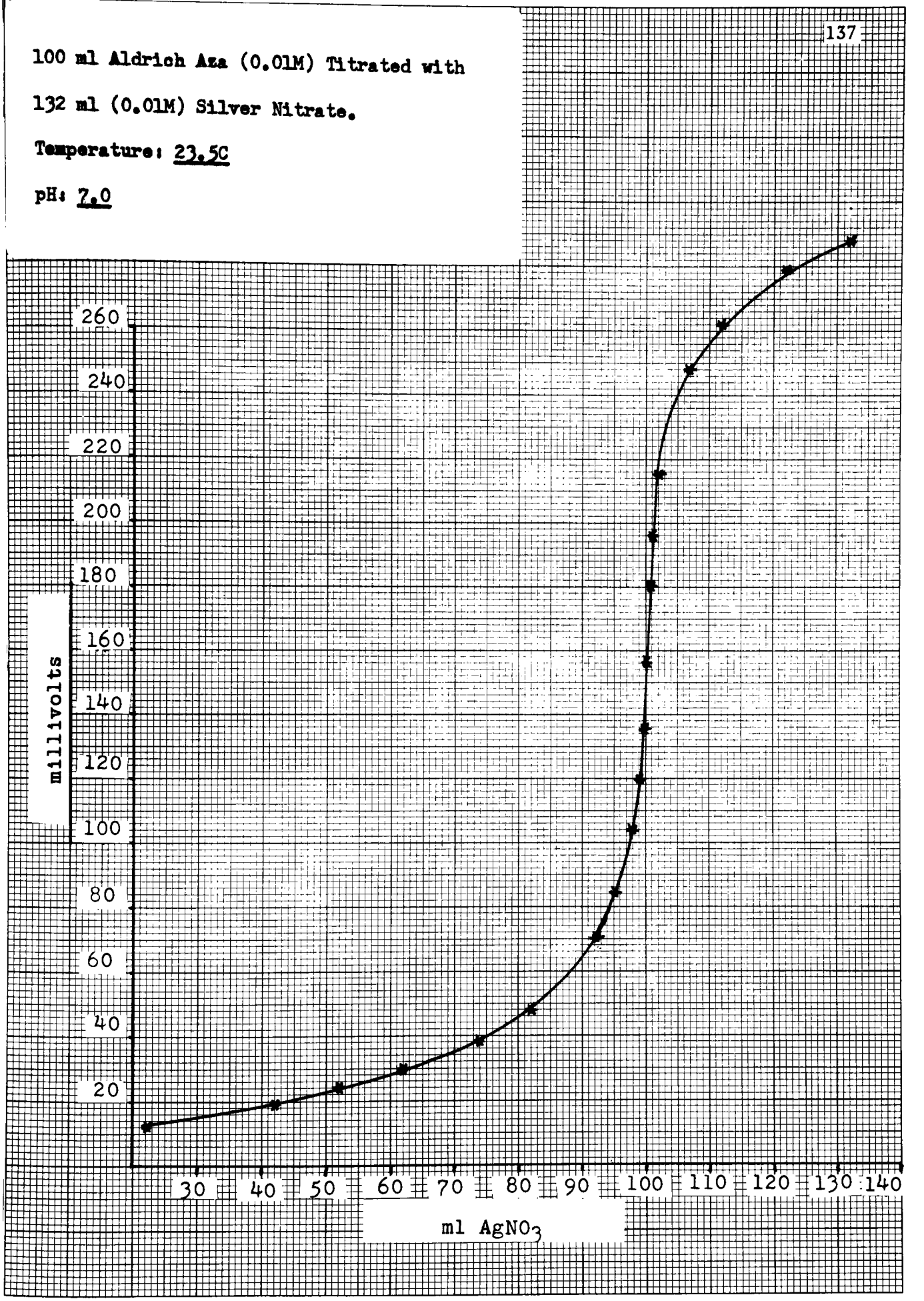

Figure 88.

100 ml Kodak Aza (0.01M) Titrated with

140 ml (0.01M) Silver Nitrate.

Temperature: 23.5C

pH: 7.0

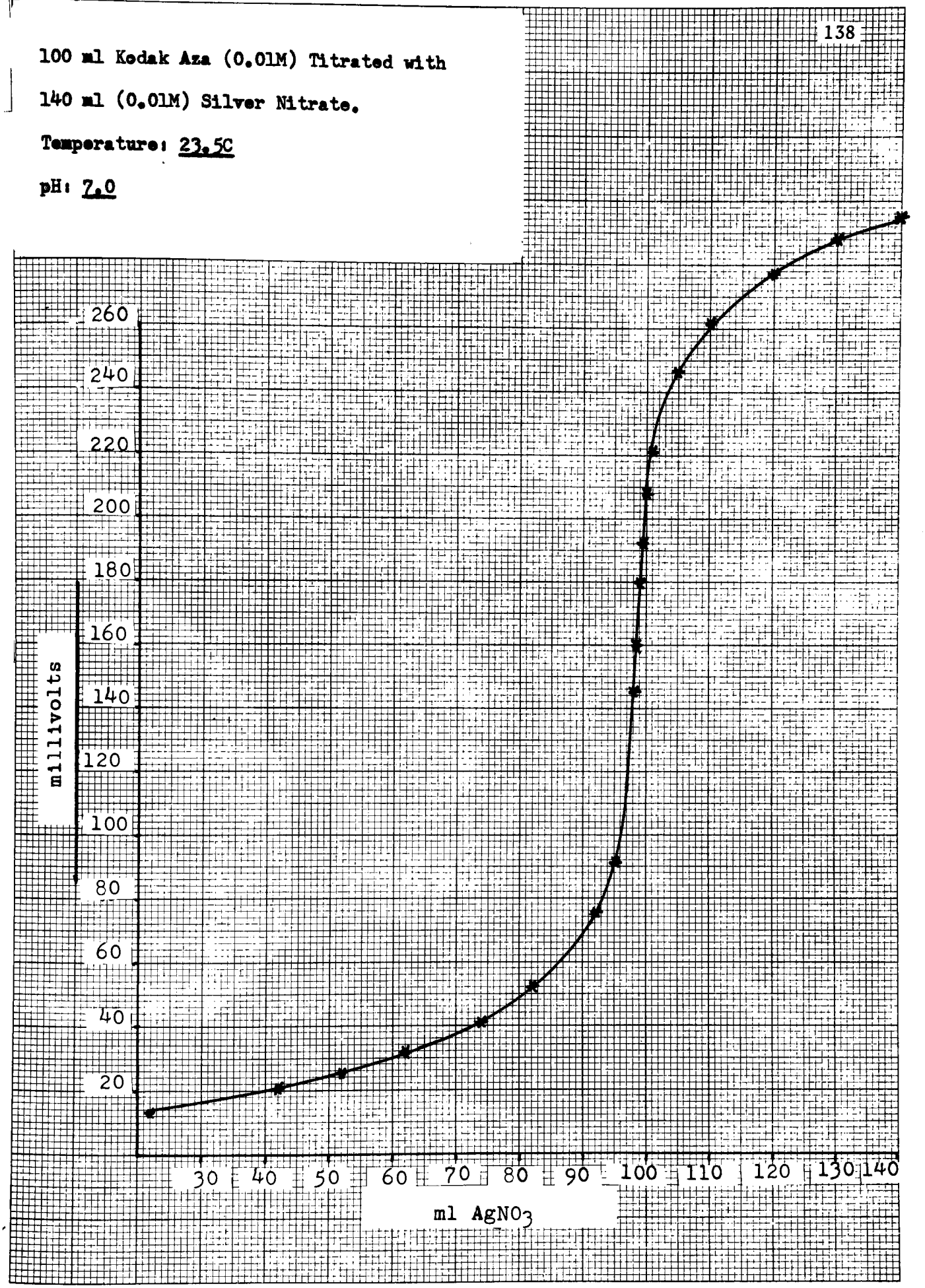

Figure 89

$$pAg = \frac{E^{o}_{Ag} - E_R - E_{cell}}{1.984 \times 10^{-4}\ T}$$

where:

$$pAg = 9.0$$

$$E^{o}_{Ag} = 0.8 \text{ volt}$$

$$T = 296.5K$$

$$E_{cell} = 0.0496 \text{ volt}$$

E_R was calculated to be 0.3204 volt.

The solubility product of the silver salt of Aza was calculated using the same equation to evaluate the pAg at the equivalence point. The potential of the cell at equivalence in both cases was very near 0.160 volt. Thus, the calculated pAg at equivalence was 5.4. This means that the silver-ion concentration was 4×10^{-6}. The solubility product, K_{sp} was then calculated as follows:

$$K_{sp} = [Ag^{+}]\ [Aza^{-}]$$

$$K_{sp} = [Ag^{+}]^2 = (4 \times 10^{-6})^2$$

$$K_{sp} = 1.6 \times 10^{-11}$$

Faerman's[39] calculations yielded a value of 3.0×10^{-11} and Birr's[18] a value of 4.5×10^{-11}.

APPENDIX B

PREPARATION OF A SILVER BROMIDE EMULSION

The following procedure outlines the preparation of the emulsion used in Section 2 of this work:

A. The following were added to a stainless steel beaker:
   (1) 15g KBr
   (2) 2.5g Gelatin
   (3) 160 ml Distilled Water
   The gelatin was allowed to soak 15 minutes.

B. The following were added to a 600 ml beaker:
   (1) 17.0g $AgNO_3$
   (2) 459 ml Distilled Water
   The $AgNO_3$ was allowed to dissolve

C. The following were added to a 1000 ml glass beaker:
   (1) 200 ml Saturated Na_2SO_4 solution
   (2) 14.3 ml (0.05 N) H_2SO_4

The steel beaker was placed in the thermostatically controlled water bath at 65C, and the solution was stirred with a small motor and glass stirrer until the gelatin dissolved. The $AgNO_3$ solution was placed in a separatory funnel filled with a capillary. Under a 1A safelight, the stopcock of the separatory funnel was opened so that all the silver nitrate solution was added in 6 minutes to "A". When precipitation was completed, solutions A and B were added to solution C, mixed well, and poured back into the metal beaker. Coagulation did not start after 1 minute, therefore solid Na_2SO_4 was added one gram at a time with vigorous hand-stirring until coagulation occurred. After coagulation,

the coagulum was allowed to settle 10 minutes undisturbed. The liquid was then slowly drained from the coagulum. The beaker was filled with cold distilled water, stirred well by hand, and allowed to settle 10 minutes then drained again. The beaker was filled half full with cold distilled water, allowed to settle, then drained again.

The following solution was prepared in a 1000 ml glass beaker for re-dispersion of the emulsion:

(1) 30g Gelatin
(2) 400 ml 5 x 10^{-4} N KBr solution
(3) 5.0 ml 0.065 N NaOH solution

The gelatin was allowed to soak 10 minutes. The beaker was placed in the thermostat at 55C and stirred to dissolve the gelatin using a small motor and glass stirrer. Under a No. 1 safelight, the emulsion beaker was opened, and the accumulated liquid was drained from the coagulum. When the gelatin was dissolved, it was poured over the coagulum, and the beaker placed in the thermostat with continued stirring for 10 minutes. The steel beaker was then covered with aluminum foil and placed in the refrigerator for future use. This emulsion contained approximately 0.10 moles AgBr.

APPENDIX C

DETERMINATION OF ABSORPTION OF DYE IN GELATIN

Three different cyanine dye concentrations were added to solutions containing the following:

(1) 30g Gelatin

(2) 400 ml 5 x 10^{-4} N KBr solution

(3) 5.0 ml 0.065 N NaOH solution

The following indicate the situations tested:

(A) 0.150g dye/430g gelatin solution

(B) 0.065g dye/430g gelatin solution

(C) 0.015g dye/430g gelatin solution

(D) 0.200g Aza added to "A".

Coatings of the 4 situations listed above were placed on 5-inch by 7-inch clear acetate sheets and allowed to dry. The transmission spectra were scanned and are shown on Figure 90.

The scans show that the dye absorbs in the gelatin matrix with maxima at 495 nm and near 530 nm. This was verified from coating "A" as the other two coatings, "B" and "C", were not concentrated enough in dye. The addition of Aza, "D", had no significant effect on the two bands. Two replicates were made in each case with no appreciable differences observed.

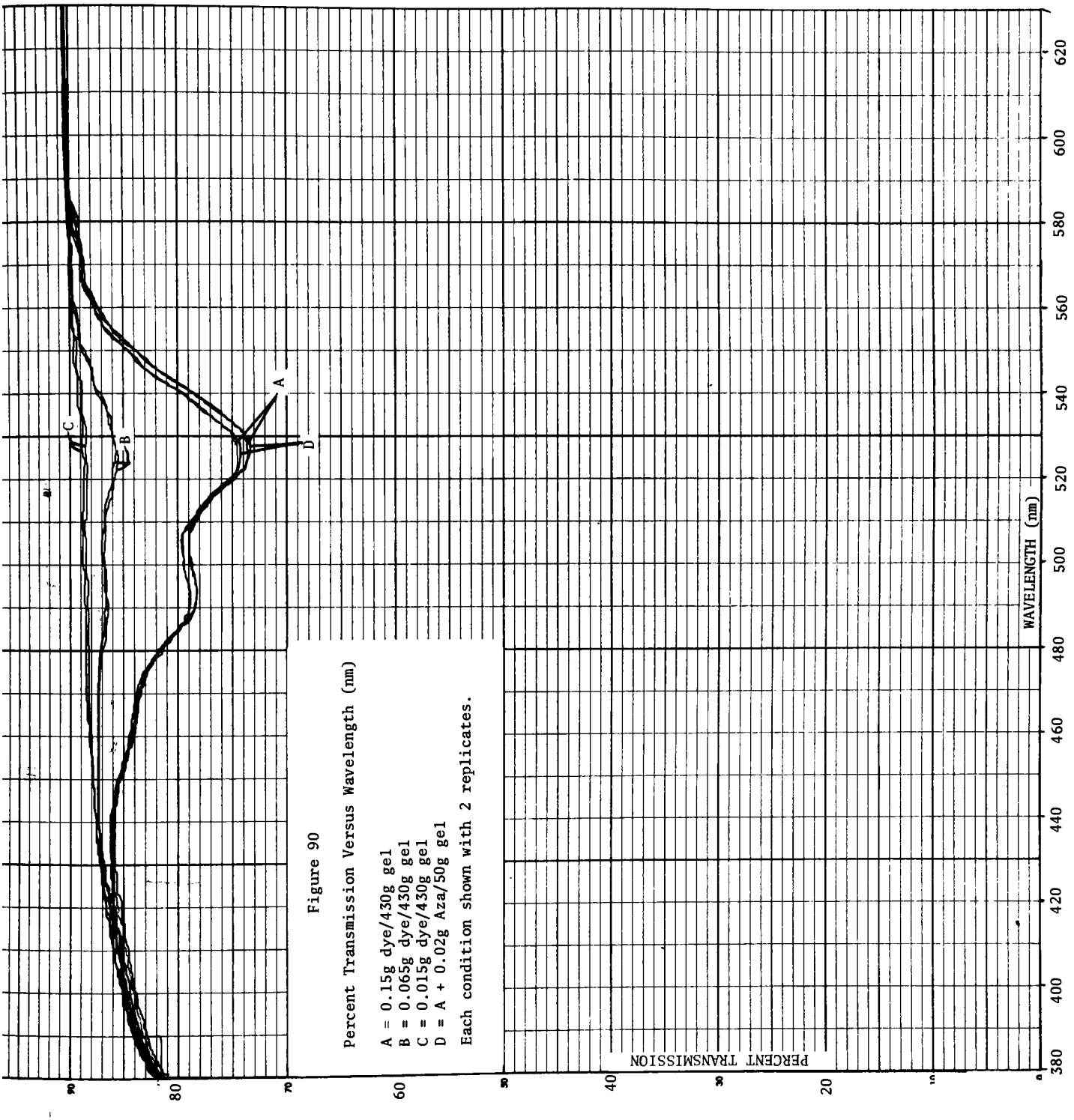
Figure 90
Percent Transmission Versus Wavelength (nm)
A = 0.15g dye/430g gel
B = 0.065g dye/430g gel
C = 0.015g dye/430g gel
D = A + 0.02g Aza/50g gel
Each condition shown with 2 replicates.
PERCENT TRANSMISSION
WAVELENGTH (nm)
A
B
C
D
380
400
420
440
460
480
500
520
540
560
580
600
620
80
60
40
20

Figure 90

APPENDIX D

SPECTRAL ANALYSIS FOR CYANINE DYE DISPLACEMENT BY AZA

Figures 91 through 93 show the reflectance and transmittance spectra of 0.15g dye/mol AgBr both wet and dry in the absence of Aza. Replicates 1 and 2 are on Figure 91. Rw and Rd represent reflectance wet and dry, respectively. Tw and Td represent transmittance wet and dry.

The spectrophotometer would occasionally hesitate before making the scan. This lag was around 2 nm when it occurred. If an obvious hesitation was observed, the scan was stopped, and a reference line was drawn at 400 nm. Other than this slight instrument lag the only other problem occurred on replicate 4 Tw. This sample came unglued from the instrument at near 535 nm, and the transmission notably decreased. The sample was promptly returned to the ice chest, and another scan was made within a few minutes.

Figures 94 and 95 show the results of five replicates of 0.15g dye/mol AgBr in the presence of 2.0g Aza/mol AgBr.

Figures 96 through 98 are the results of the same dye concentration in the presence of 0.2g Aza/mol AgBr. Nine replicates were made, however only six were used. No. 1 was discarded because it had too many air bubbles in the emulsion. No. 6 was not used, because it was allowed to stand too long wet. No. 9 was not used, because it was accidentally contaminated.

Figure 99 shows the results of using 3.0g Aza/mol AgBr. Only two replicates were made just to determine if the J-band strength was materially different from its value with 2g Aza/mol AgBr. The results show that it was not.

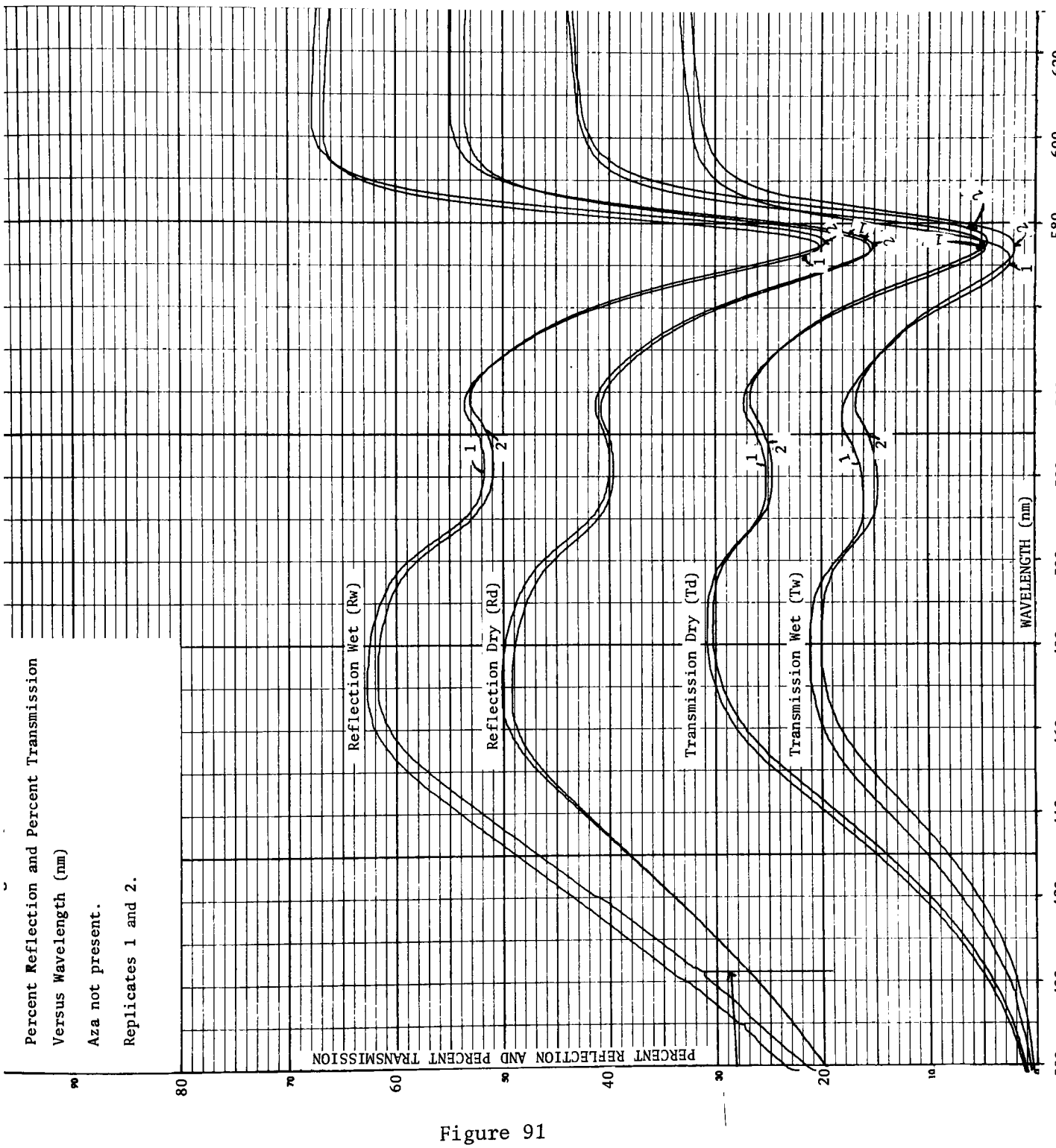
Percent Reflection and Percent Transmission
Versus Wavelength (nm)
Aza not present.
Replicates 1 and 2.
Reflection Wet (Rw)
Reflection Dry (Rd)
Transmission Dry (Td)
Transmission Wet (Tw)
PERCENT REFLECTION AND PERCENT TRANSMISSION
WAVELENGTH (nm)
380
400
420
440
460
480
500
520
540
560
580
600
620
20
40
60
80

Figure 91

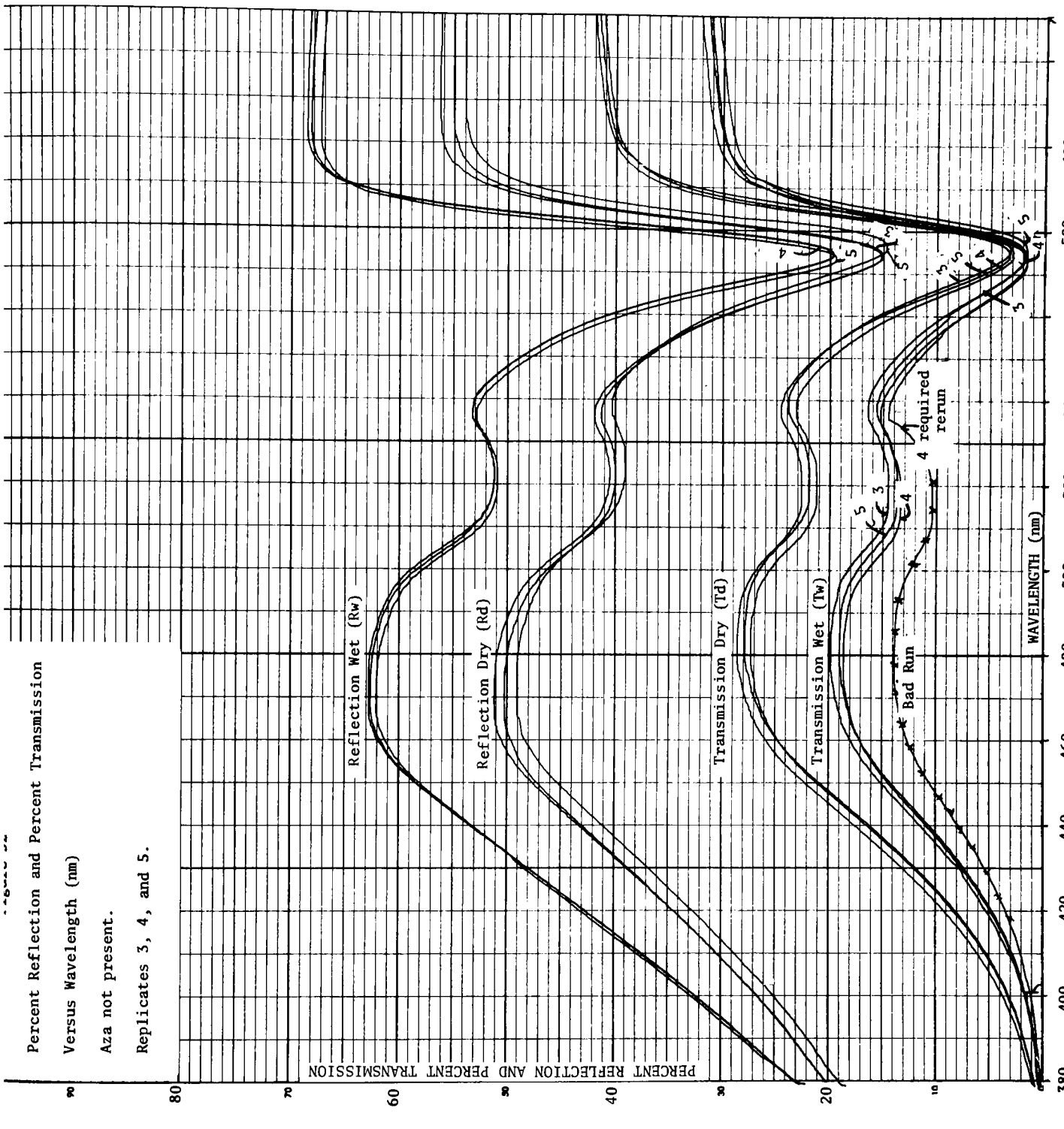
Percent Reflection and Percent Transmission
Versus Wavelength (nm)
Aza not present.
Replicates 3, 4, and 5.
Reflection Wet (Rw)
Reflection Dry (Rd)
Transmission Dry (Td)
Transmission Wet (Tw)
Bad Run
4 required rerun
PERCENT REFLECTION AND PERCENT TRANSMISSION
WAVELENGTH (nm)
80
70
60
50
40
30
20
10
380
400
420
440
460
480
500
520
540
560
580
600
620

Figure 92

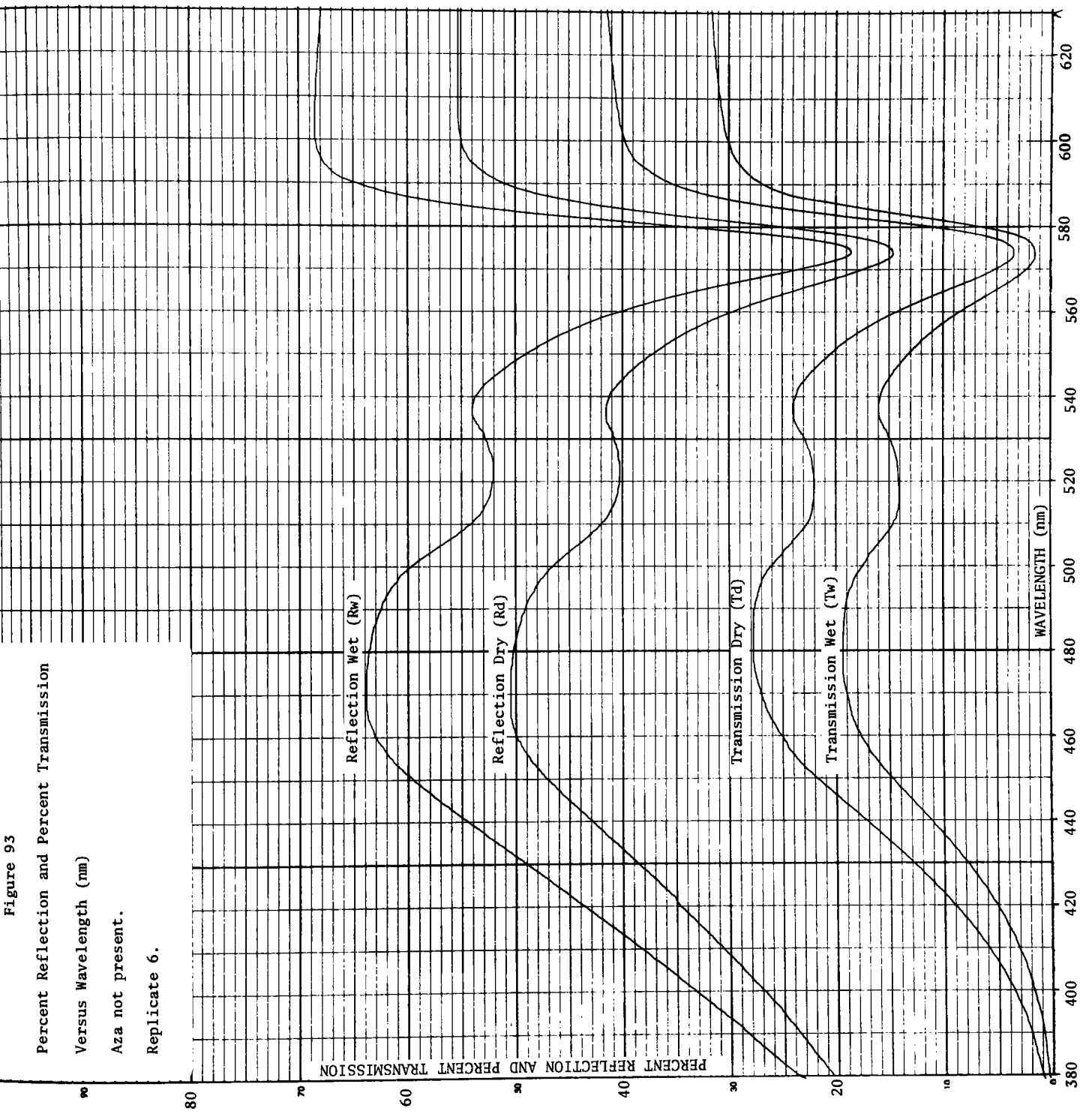
Figure 93
Percent Reflection and Percent Transmission
Versus Wavelength (nm)
Aza not present.
Replicate 6.
Reflection Wet (Rw)
Reflection Dry (Rd)
Transmission Dry (Td)
Transmission Wet (Tw)
PERCENT REFLECTION AND PERCENT TRANSMISSION
WAVELENGTH (nm)
80
70
60
50
40
30
20
10
0
380
400
420
440
460
480
500
520
540
560
580
600
620

Figure 93

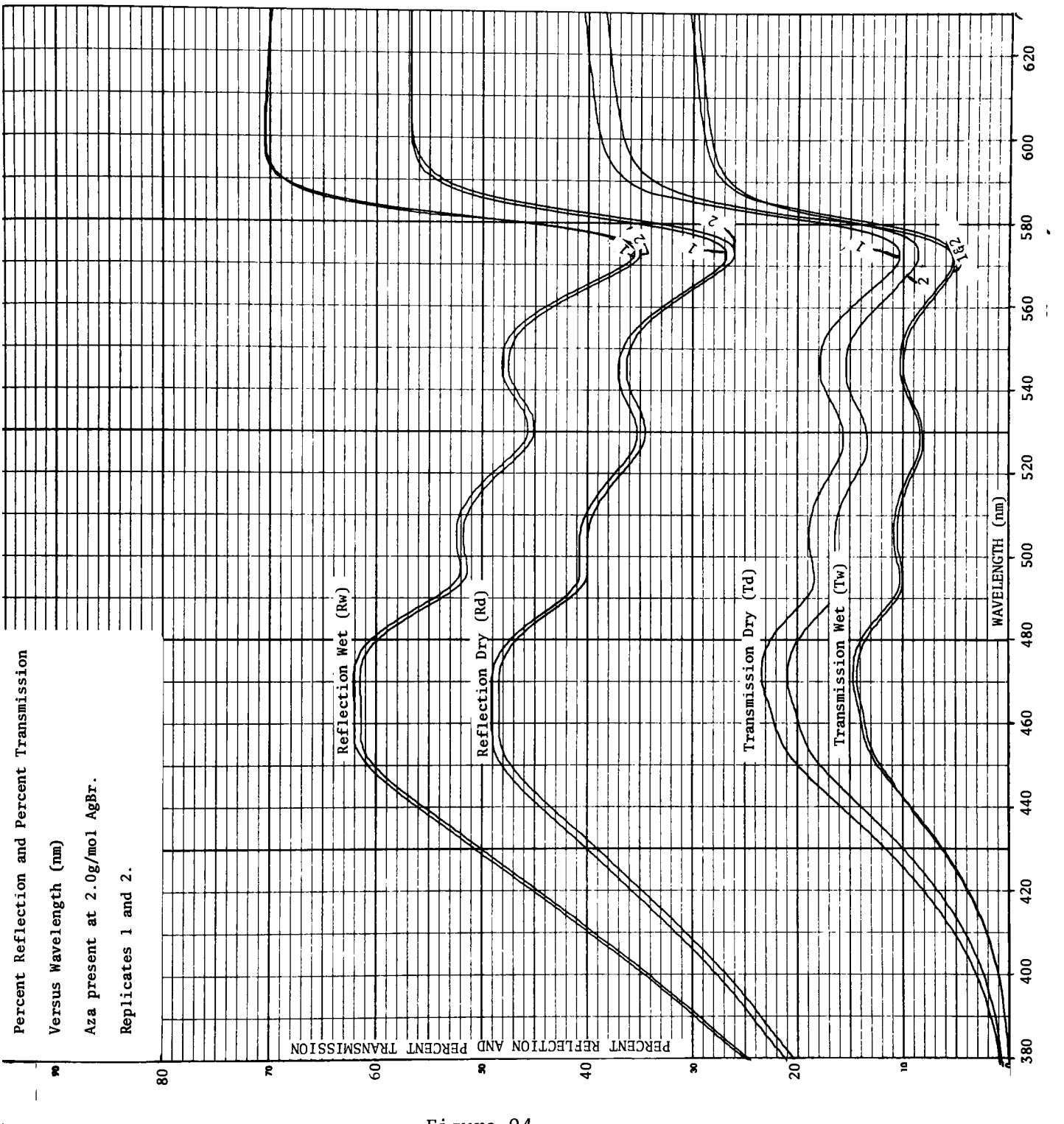
Percent Reflection and Percent Transmission
Versus Wavelength (nm)
Aza present at 2.0g/mol AgBr.
Replicates 1 and 2.
Reflection Wet (Rw)
Reflection Dry (Rd)
Transmission Dry (Td)
Transmission Wet (Tw)
PERCENT REFLECTION AND PERCENT TRANSMISSION
WAVELENGTH (nm)
80
70
60
50
40
30
20
10
380
400
420
440
460
480
500
520
540
560
580
600
620

Figure 94

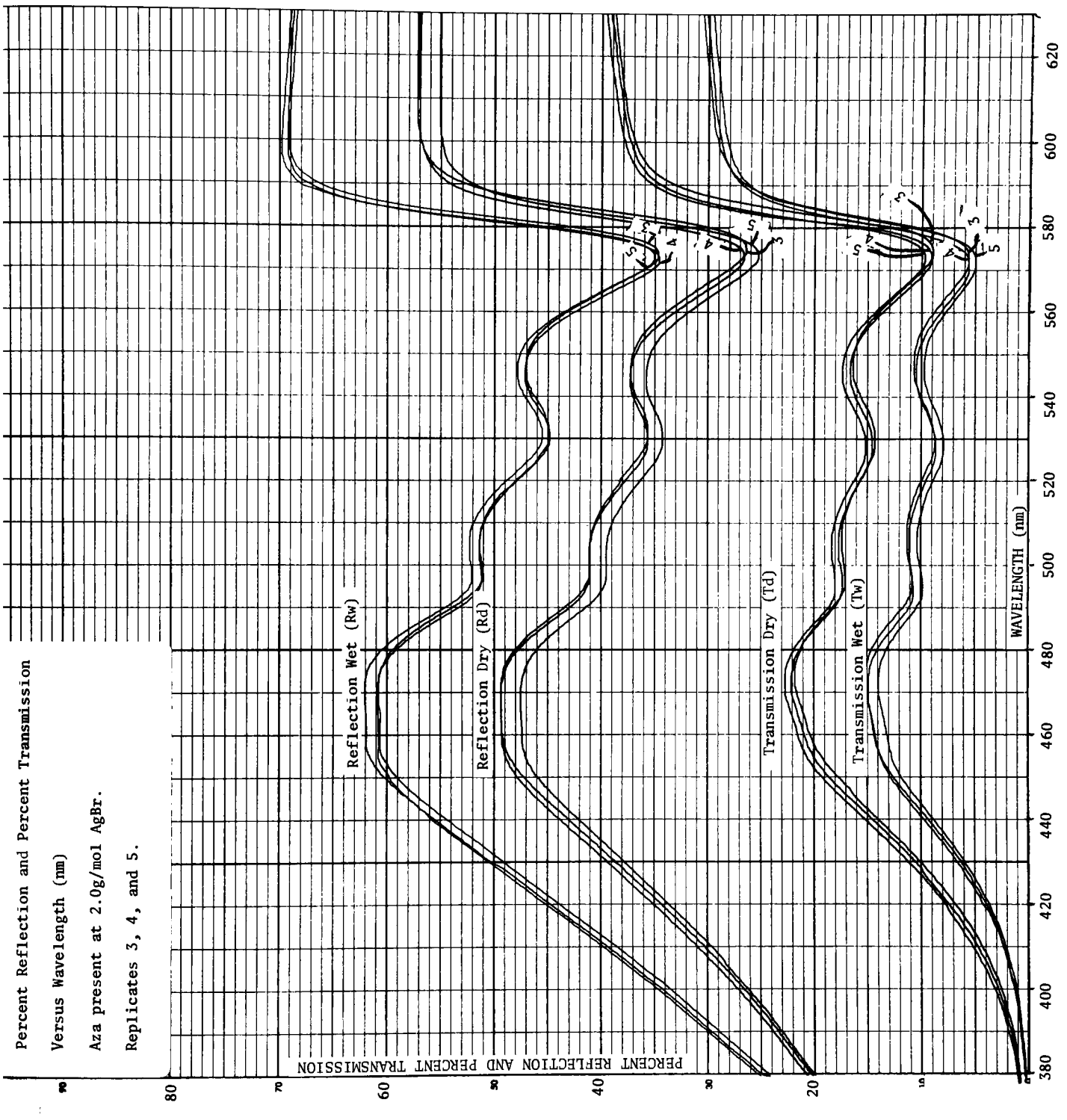
Percent Reflection and Percent Transmission
Versus Wavelength (nm)
Aza present at 2.0g/mol AgBr.
Replicates 3, 4, and 5.
Reflection Wet (Rw)
Reflection Dry (Rd)
Transmission Dry (Td)
Transmission Wet (Tw)
PERCENT REFLECTION AND PERCENT TRANSMISSION
WAVELENGTH (nm)
80
60
40
20
380
400
420
440
460
480
500
520
540
560
580
600
620

Figure 95

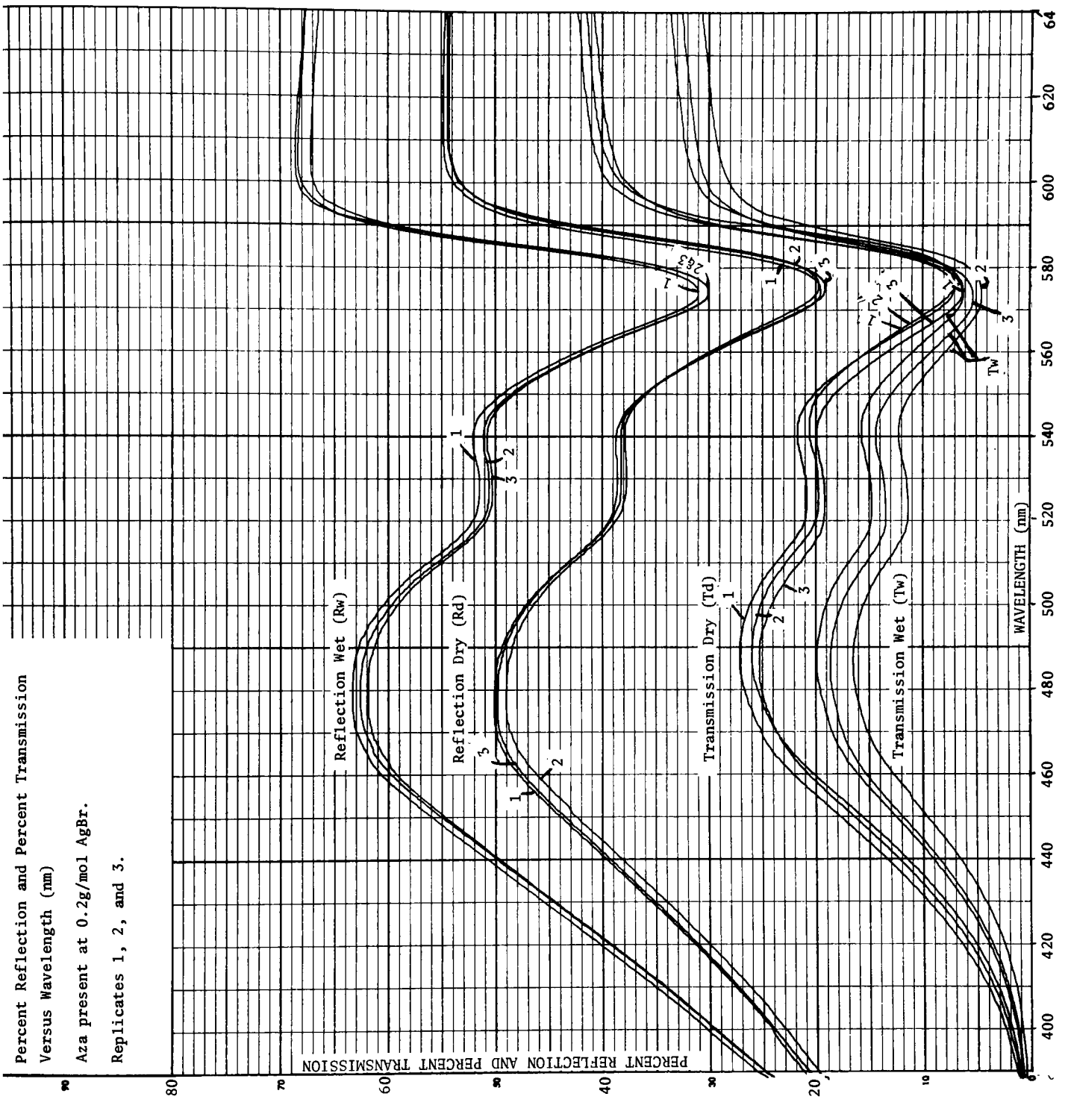
Percent Reflection and Percent Transmission
Versus Wavelength (nm)
Aza present at 0.2g/mol AgBr.
Replicates 1, 2, and 3.
Reflection Wet (Rw)
Reflection Dry (Rd)
Transmission Dry (Td)
Transmission Wet (Tw)
PERCENT REFLECTION AND PERCENT TRANSMISSION
WAVELENGTH (nm)
80
70
60
50
40
30
20
10
0
400
420
440
460
480
500
520
540
560
580
600
620
640

Figure 96

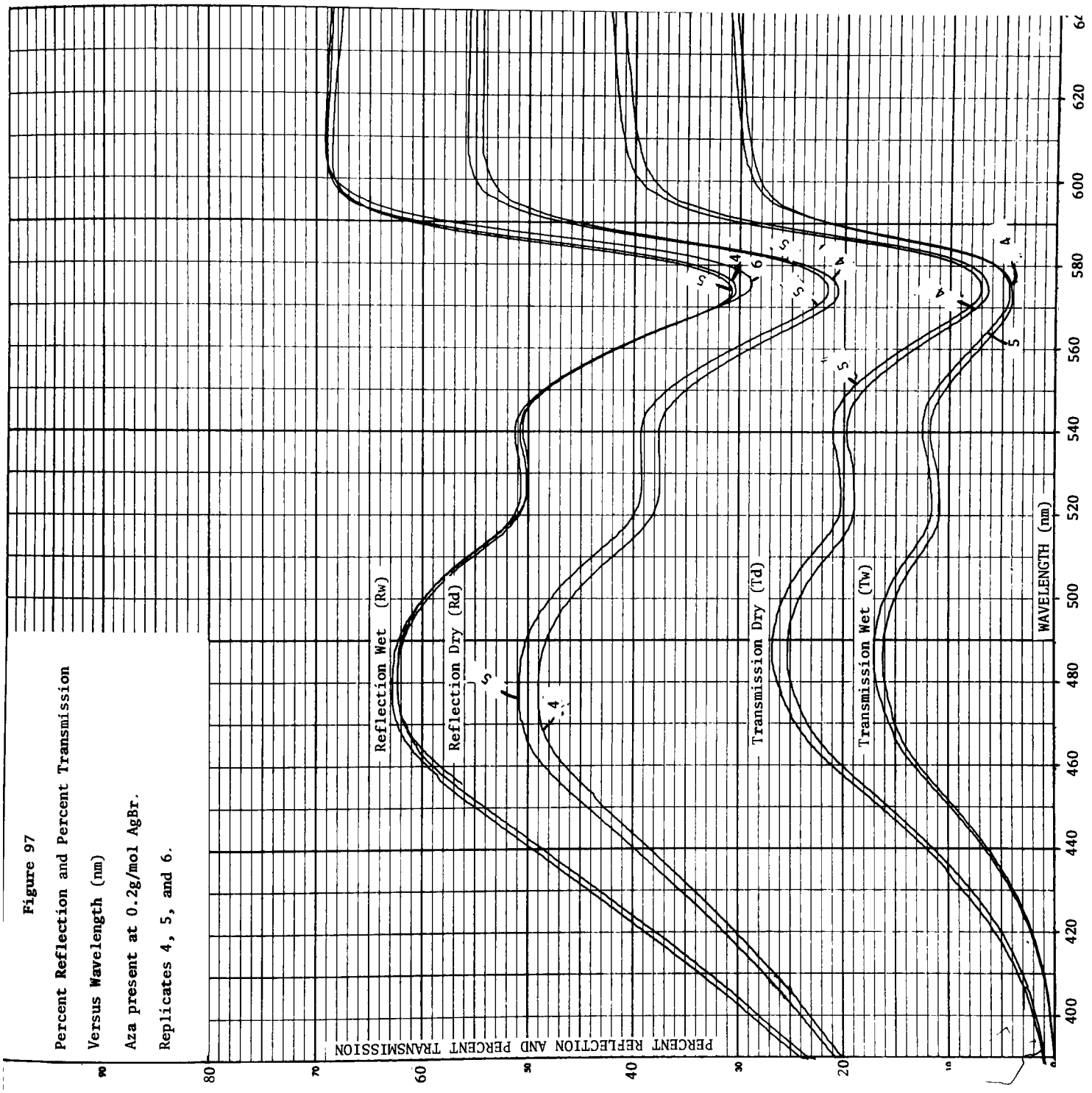
Figure 97
Percent Reflection and Percent Transmission
Versus Wavelength (nm)
Aza present at 0.2g/mol AgBr.
Replicates 4, 5, and 6.
Reflection Wet (Rw)
Reflection Dry (Rd)
Transmission Dry (Td)
Transmission Wet (Tw)
PERCENT REFLECTION AND PERCENT TRANSMISSION
WAVELENGTH (nm)
80
70
60
50
40
30
20
400
420
440
460
480
500
520
540
560
580
600
620

Figure 97

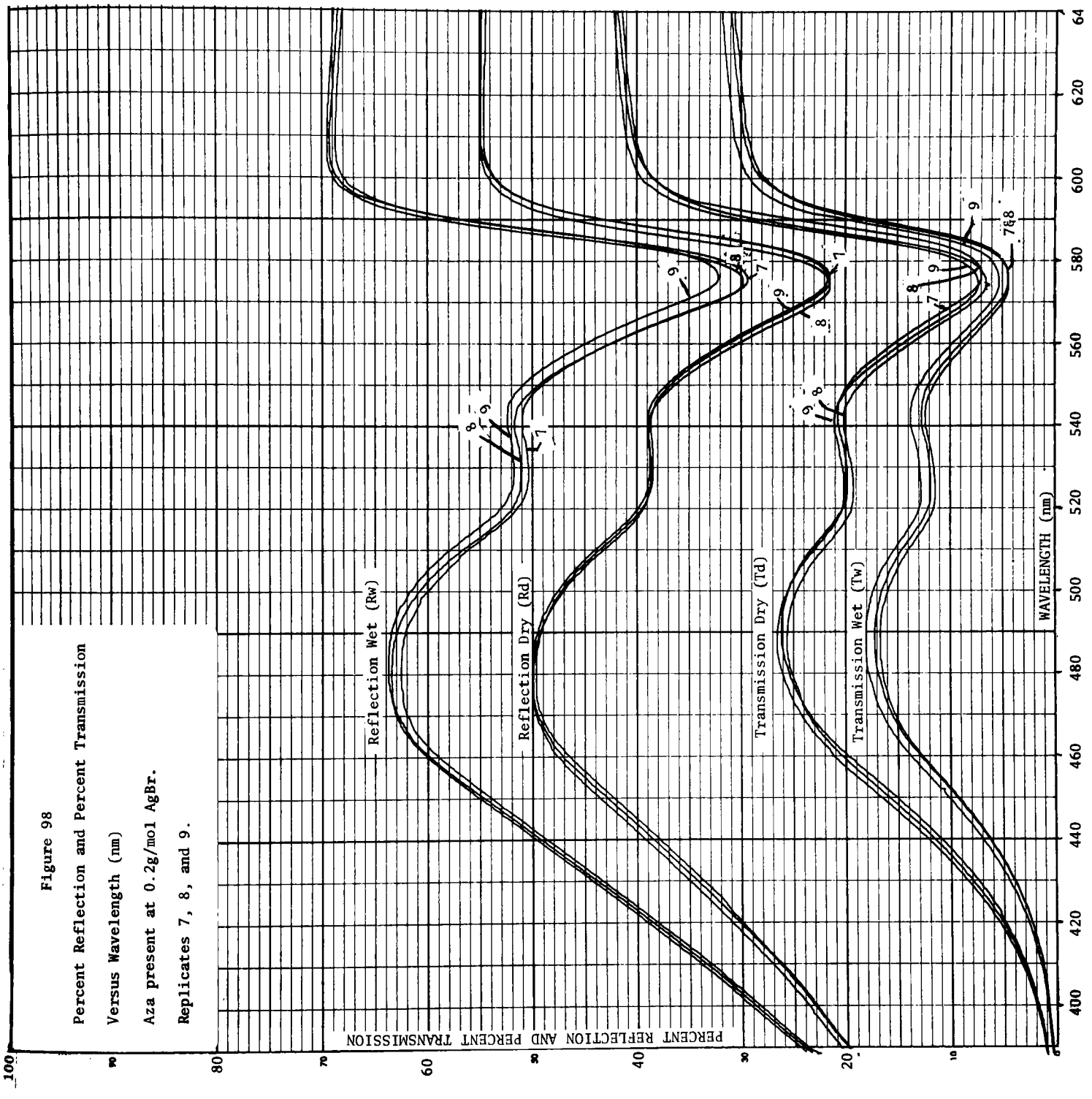
Figure 98
Percent Reflection and Percent Transmission
Versus Wavelength (nm)
Aza present at 0.2g/mol AgBr.
Replicates 7, 8, and 9.
Reflection Wet (Rw)
Reflection Dry (Rd)
Transmission Dry (Td)
Transmission Wet (Tw)
PERCENT REFLECTION AND PERCENT TRANSMISSION
WAVELENGTH (nm)
100
80
60
40
20
400
420
440
460
480
500
520
540
560
580
600
620
640

Figure 98

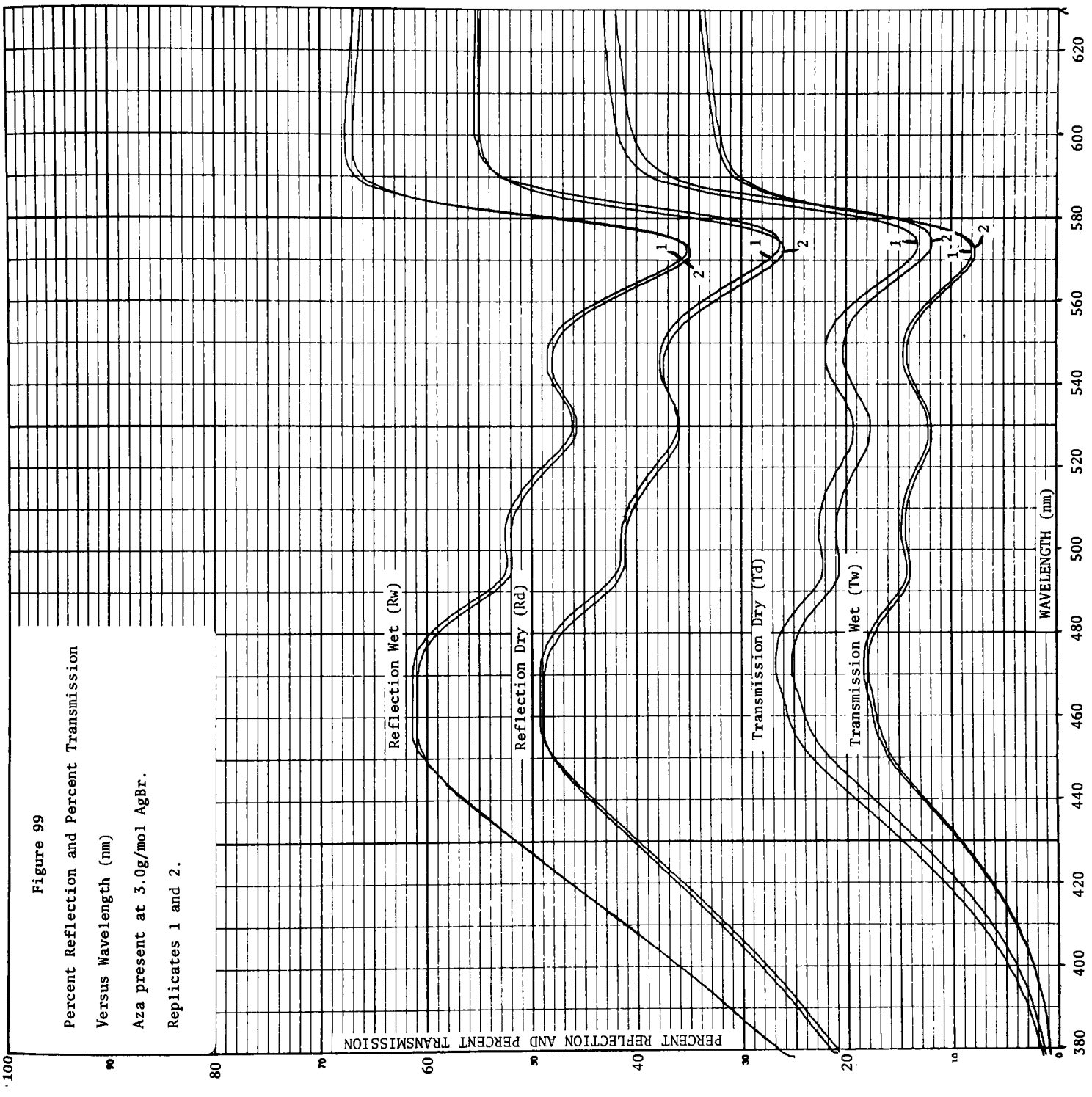
Figure 99
Percent Reflection and Percent Transmission
Versus Wavelength (nm)
Aza present at 3.0g/mol AgBr.
Replicates 1 and 2.
Reflection Wet (Rw)
Reflection Dry (Rd)
Transmission Dry (Td)
Transmission Wet (Tw)
PERCENT REFLECTION AND PERCENT TRANSMISSION
WAVELENGTH (nm)
100
80
60
40
20
0
380
400
420
440
460
480
500
520
540
560
580
600
620
1
2

Figure 99

APPENDIX E

SOLUBILITY OF CYANINE DYE IN WATER IN THE PRESENCE AND THE ABSENCE OF AZA

Because Aza dissolves in polar solvents and cyanine dye is more soluble in non-polar solvents, a partition distribution of dye in the aqueous phase in the presence and the absence of varying concentrations of Aza was determined. The peak absorbance of the dye in water is at 520 nm, therefore the Bausch and Lomb Spectronic 20 Spectrophotometer used for the analysis was set and maintained at that wavelength.

0.005g of dye was dissolved in 100 ml methylene chloride. Three concentrations of Aza were used: (1) 2.1×10^{-3} m/l, (2) 8.4×10^{-3} m/l, and (3) 3.36×10^{-3} m/l. Control was obtained as follows: (1) 25 ml of the dye in methylene chloride and 25 ml of distilled water were placed in a separatory funnel, (2) the solutions were shaken thoroughly until the dye reached equilibrium between both layers, (3) the solutions were separated, (4) the aqueous phase was then diluted 10:1 and read on the spectrophotometer at 420 nm with distilled water as the blank. This process was repeated for each of the three concentrations of Aza. The following absorbance values are the results of the four cases under test:

(1) Control - 0.45 absorbance

(2) Aza at 2.1×10^{-3} m/l - 0.48 absorbance

(3) Aza at 8.4×10^{-3} m/l - 0.46 absorbance

(4) Aza at 3.36×10^{-3} m/l - 0.71 absorbance. Since the aqueous phase did not clear completely, it was centrifuged. After centrifuging the absorbance was 0.60.

The first three values are essentially equivalent, within experimental error. Since absorbance is proportional to concentration, the results indicate that Aza had no influence on the solubility of the dye in the aqueous phase when present in concentrations up to 8.4×10^{-3} m/l. This concentration of Aza was not exceeded in the dye displacement study.